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PROCEEDINGS

OF THE

NATIONAL INSTITUTE OF SCIENCES OF INDIA

19389
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VOL. VI

1940

I.A.R.I. RES. INST.

CALCUTTA
PUBLISHED BY THE NATIONAL INSTITUTE OF SCIENCES OF INDIA

19389

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Fifth Annual General Meeting.

The Fifth Annual General Meeting of the National Institute of Sciences of India was held at 11 A M on Tuesday, the 2nd January 1940, in the North Eastern Lecture Hall of the Medical College, Madras

The following Fellows were present —

Bt Col R N Chopra, *President*, in the Chair
Rao Bahadur B Viswa Nath, *Additional Vice President*
Prof S P Agharkar *Honorary Secretary*

Dr Nazir Ahmad
Prof A C Banerji
Prof Y Bharadwaja
Prof F R Bharucha
Mr T P Bhaskara Shastri
Dr H Chaudhuri
Capt S Datta
Prof S Datta
Prof S C Dhar
Dr Gilbert J Fowler
Prof J C Ghosh
Dr F H Gravely
Dr P C Guha
Dr D S Kothari
Dr S Krishna
Dr M S Krishnan
Prof S K Mitra
Prof P C Mitter
Prof P Neogi
Dr C G Pandit.
Dr M Prasad
Dr H S Pruthi
Rao Bahadur G N Rangaswami Ayyangar
Dr B Rama Rao
Prof L Rama Rao
Prof J N Ray
Dr H K Sen
Sir S M Sulaiman
Rao Bahadur T S Tirumurti
Dr K Venkataraman
Rao Bahadur T S Venkataraman

The meeting was also attended by 64 visitors

1 The minutes of the Twelfth Ordinary General Meeting were read and confirmed

2 The President appointed Dr F H Gravely and Prof J C Ghosh to act as scrutineers of the ballot papers received for the election of officers and other members of Council for the year 1940

3 The following Ordinary Fellows signed the duplicate obligation and were admitted Fellows as per Rule 13

Prof F R Bharucha
Capt S Datta
Prof L Rama Rao
Dr C G Pandit
Dr K Venkataraman

4 The following were declared elected officers and other members of the Council for the year 1940 —

President Bt Col R N Chopra
Vice-Presidents Sir U N Brahmachari
Dr A M Heron
Treasurer Dr B S Guha
Foreign Secretary Prof J C Ghosh
Secretaries Prof S P Agharkar
Dr C. S Fox

Members of Council —

Dr S L Hora
Khan Bahadur M Afzal Husain
Dr M S Krishnan
Dr R B Lal
Prof G Matthai
Prof J N Mukherjee
Dr C W B Normand
Prof G R Paranjpe
Principal P Parija
Dr B Prashad
Prof M Qureshi
Rao Bahadur G N Rangaswami Ayyangar
Prof N R Sen
Sir Shah M Sulaiman
Col J Taylor
Rao Bahadur B Venkatesachar
Mr F Ware

5 The Annual Report for the year 1939, prepared by the Council, was adopted

6 The following papers were read —

(1) An attempt to neutralize the space-charge of a hot filament by fast positive ions of mercury Part I By R M Chaudhry, S M Nawas and M Aslam (Communicated by Sir S M Sulaiman)

(2) A contribution to the Morphology of *Carthamus tinctorius* Linn By I Banerji (Communicated by Prof S P Agharkar)

(3) Studies in the Isoquinoline Series Parts IV–VII By B B Dev and collaborators

(4) On the Photo-ionization of Molecules By B D Nag-Chowdhury and K Bose (Communicated by Prof M N Saha)

(5) Studies on the Chemistry and Biology of the Slow Sand Filters at the Madras Water Works By S V Ganapati (Communicated by Dr Gilbert J Fowler)

7 The President delivered his Annual Address The address will be printed in the 'Proceedings'

With a vote of thanks to the Chair the meeting terminated

National Institute of Sciences of India.

ANNUAL REPORT

The Council of the National Institute of Sciences of India have pleasure in submitting the following report on the general concerns of the Institute for the year 1939, as required by the provisions of rule 48(*f*)

Membership

The number of Fellows on the roll of the Institute at the beginning of the year was 157 Ordinary Fellows and 17 Honorary Fellows 11 Ordinary Fellows and 4 Honorary Fellows were elected during the year in accordance with the procedure laid down in the Regulations 3 Ordinary Fellows resigned their Fellowship during the year The total number of Fellows on the roll at the end of the year is 165 Ordinary Fellows and 21 Honorary Fellows Of the 165 Ordinary Fellows 7 are non-resident

Meetings

The fourth Annual Meeting was held in the Hailey Hall, Lahore, on the 2nd January, 1939 An account of the meeting was published in the *Proceedings*, Vol V, No 1, pp 1-2

Two Ordinary General Meetings were held during the year Both meetings were held in Calcutta in the rooms of the Royal Asiatic Society of Bengal, the first on the 5th April, 1939 and the second on the 25th and 26th August, 1939 The latter meeting included a Symposium on 'Coal in India' Accounts of these meetings, together with the papers read, are being published in the *Proceedings* Two of the papers have been published in the *Transactions*

The Council

The officers and members of Council for the year 1939 were elected at the fourth Annual Meeting held on the 2nd January, 1939 The Council, together with the representatives of the co-operating Academies, the Indian Science Congress Association and the Government of India, was constituted as follows —

President	Bt Col R N Chopra
Vice Presidents	Sir U N Brahmachari Dr A M Heron
Additional Vice Presidents	Prof J N Mukherjee Prof M N Saha Rao Bahadur B Viswanath
Treasurer	Dr B S Guha

Foreign Secretary	Prof B Sahni	
Secretaries	Prof S P Agharkar	
	Dr C S Fox	
Members of Council	Prof S S Bhatnagar	
	Mr H G Champion	
	Prof J C Ghosh	
	Khan Bahadur M Afzal Husain	
	Dr M S Krishnan	
	Dr R B Lal	
	Prof S K Mitra	
	Dr C W B Normand	
	Prof G R Paranjpe	
	Dr Baini Prashad	
	Prof M Qureshi	
	Rao Bahadur G N Rangaswami Ayyangar	
	Prof N R Sen	
	The Hon'ble Sir Shah M Sulaiman	
	Col J Taylor	
	Rao Bahadur B Venkatesachar	
	Mr F Ware	
	Brigadier Sir Harold Couchman	(*Ex-officio*)
	Sir Lewis Fermor	
Additional Members of Council	Prof A C Banerji	
	Sir Bryce Burt	
	Prof R Gopala Aiyar	
	Principal P Parija	

The Council held seven meetings and one emergency meeting during the year

Committees

A sub-committee consisting of the President, the Secretaries, Dr R B Lal and Prof M N Saha was appointed to consider the replies received on the questionnaire on Science and its Social Relations and to prepare a report thereon

The Sectional Committees are given in Appendix III

Delegates to Foreign Congress

Col Sir Arthur Olver was appointed to represent the National Institute at the 7th International Congress of Genetics to be held at Edinburgh

Dr A M Heron, Prof B Sahni and Mr D N Wadia were appointed delegates to the 18th International Geological Congress to be held in London in 1940

Publications

Three numbers of the *Proceedings*, two numbers of the *Transactions* and three numbers of *Indian Science Abstracts* were published during the year.

Exchanges.

Six additional Institutions were placed on the exchange list for the publications of the Institute, bringing the total number on the list to ninety-one (*vide* Appendix IV).

Library

Four hundred and forty-one books, parts of periodicals and reprints were added to the library during the year (*vide* Appendix V)

Presents and Donations

The following grants-in-aid have been sanctioned during the year to the Institute --

(1) Rs 500 from the Calcutta University for the session 1939-40
(2) Rs 300 from the Osmania University for the year 1348 F

Finance

An audited statement of accounts of the National Institute for the period from 1st December, 1938 to 30th November, 1939 is submitted (*vide* Appendix VI) The total ordinary receipts for this period are Rs 14,821-1-4 (inclusive of the grant-in-aid of Rs 6,000 from the Government of India), and the ordinary payments Rs 17,533-11-6, showing an excess of payments over receipts of Rs 2,712-10-2 A sum of Rs 256 was realized on account of admission fees and Rs 274-2-0 on account of compounding subscription

At the beginning of the year the cash position of the Institute was as follows

	Rs	A	P
In Savings Bank account	2,145	2	0
,, Government paper	33,000	0	0
Current account	12,023	15	8
,, Hand	6	15	9
TOTAL	47,176	1	5

At the end of the year, however, the cash position was reduced to the amount as shown below

	Rs	A	P
In Savings Bank account	2,166	7	0
,, Government paper	40,000	0	0
,, Current account	2,079	5	3
,, Hand	12	13	0
TOTAL	44,258	9	3

APPENDICES

I List of Fellows
II Abstract Proceedings of the Council
III Committees, 1940
IV List of Institutions on the exchange list
V Periodicals received for the Library
VI Audited statement of accounts, December 1938–November 1939
VII Budget Estimate, December 1939–November 1940

APPENDIX I

LIST OF FELLOWS

ORDINARY FELLOWS

1 **Abraham**, Lt Col W E V, A R C S (I), F G S, M Inst P T, Senior Geologist Burmah Oil Co Ltd, Burma, Khodaung, Magwe, Burma (1936)

2 **Agharkar**, S P, M A, Ph D, F L S, Ghose Professor of Botany, Calcutta University 35, Ballygunj Circular Road, Calcutta

3 **Ahmad**, **Nazir**, O B E, M Sc, Ph D, Director, Indian Central Cotton Committee's Technological Laboratory, Matunga, Bombay

4 **Aiyar**, R **Gopala**, M A, L T, M Sc, University Professor of Zoology and Director, University Zoological Laboratory, Madras (1938)

5 **Ajrekar**, S L, B A, I E S (Retd) 855 Bhamburda, Poona 4

6 **Ananda Rao**, K Rao Bahadur, M A, I E S, Professor of Mathematics, Presidency College, Madras

7 **Ash**, W C, B Sc, M Inst C E, A M I Mech E, Bengal Club, Calcutta

8 **Auden**, J B, M A (Cantab) Geologist Geological Survey of India, Indian Museum Calcutta (1938)

9 **Awati**, P R, B A, D I C, I E S, Professor of Zoology, Royal Institute of Science Mayo Road Bombay 1

10 **Bagchee**, K D, D Sc, D I C, Mycologist, Imperial Forest Research Institute, Dehra Dun, U P

11 **Bahl**, K N, D Sc, D Phil, Professor of Zoology, Lucknow University, Lucknow

12 **Banerjee**, K, D Sc, Reader in Physics, Dacca University, Ramna, Dacca (1939)

13 **Banerji**, A C, M Sc, M A, F R A S, I E S Professor of Mathematics, Allahabad University, Allahabad

14 **Banerji**, S K, D Sc, Meteorologist, Meteorological Office, Poona 5

15 **Beeson**, C F C, D Sc Forest Entomologist, Imperial Forest Research Institute Dehra Dun, U P

16 **Bharadwaja**, Y, M Sc, Ph D (Lond), F L S, Professor of Botany and Head of the Department, Benares Hindu University, Benares (1937)

17 **Bharucha**, F R, B A, B Sc, M Sc, D Sc, Professor of Botany and Head of the Department, Royal Institute of Science, Bombay (1939)

18 **Bhaskara Shastri**, T P, M A, F R A S, Director, Nizamiah Observatory, Hyderabad (Deccan)

19 **Bhatia**, B L, D Sc, F Z S, F R M S, F A Sc, Principal, Ranbir College, Sangrur, Jind State (1937)

20 **Bhatnagar**, S S, O B E, D Sc, Professor of Chemistry and Director, University Chemical Laboratories Panjab University, Lahore

21 **Bhattacharya**, D R, M Sc, Ph D, Dr ès Sciences (Paris) Professor of Zoology, Allahabad University, 7, Malaviya Road, Allahabad

22 **Bomford**, **Major Guy**, R E, Survey of India, Dehra Dun (1935)

23 **Bose**, D M, M A, B Sc Ph D, Director, Bose Institute, 93, Upper Circular Road, Calcutta

24 **Bose**, G S, D Sc, M B, Head of the Department of Experimental Psychology, Calcutta University, 92, Upper Circular Road, Calcutta

25 **Bose**, N K, M Sc, Ph D, Offg Director, Punjab Irrigation Research Institute, Lahore (1938)

26 **Bose**, S N, M Sc, Professor of Physics and Head of the Department, Dacca University, Ramna, Dacca

27 Bose, S R, M A, Ph D F R S E Professor of Botany, Carmichael Medical College, Calcutta (1935)

28 Brahmachari, Sir U N, Kt, Rai Bahadur, M A M D, Ph D, F R A S B, K I H Physician Medical College Hospitals Calcutta (Retired) 19, Loudon Street Calcutta

29 Burns W, D Sc, I A S, Agricultural Commissioner with the Government of India New Delhi (1935)

30 Burridge W D M M A (Oxon), Professor of Physiology Lucknow University, Lucknow

31 Burt, Sir Bryce C, Kt, C I E, M B E B Sc I A S, c/o Westminster Bank, Bishopston Bristol

32 Calder C C, B Sc (Agr), F L S, 18 Gladstone Place, Aberdeen Scotland

33 Chakravarti, S N, D Sc (Oxon), F I C F C S Chemical Examiner to Governments of U P and C P 45 Taj Road, Agra (1935)

34 Champion H G M A, Conservator of Forests Western Circle United Provinces, Naini Tal

35 Chatterjee G, M Sc, Meteorologist in charge Upper Air Observatory Agra (1935)

36 Chaudhuri H, D Sc Ph D, D I C, Head of the Department of University Teaching in Botany and Director, Kashyap Research Laboratory, Panjab University, Lahore

37 Chopra B N, D Sc F L S Assistant Superintendent, Zoological Survey of India Indian Museum Calcutta (1935)

38 Chopra, Brevet Col R N, C I E M D, Sc D F R A S B, F R C P, I M S (Retd), Director, School of Tropical Medicine Calcutta

39 Chowdhury J K M Sc Dr Phil (Berlin), Reader in Chemistry Dacca University, Ramna Dacca (1938)

40 Colchman Brigadier Sir Harold, Kt, D S O M C c/o Lloyds Bank Ltd, R Dept 6 Pall Mall, London, S W 1

41 Coulson, A L, D Sc, D I C, F G S, Superintending Geologist, Geological Survey of India Indian Museum Calcutta (1935)

42 Crookshank, H, B A, D Sc, B A I, Superintending Geologist, Geological Survey of India, Indian Museum, Calcutta (1938)

43 Dastur, R H, M Sc, Cotton Physiologist, Agricultural College, Lyallpur, Punjab

44 Datta S, M Sc D Sc, D I C, Professor of Physics, Presidency College, Calcutta (1935)

45 Datta, Captain S C A, B Sc, M R C V S, D T V M, Veterinary Research Officer, Imperial Veterinary Research Institute, Muktesar Kumaun, U P (1938)

46 Dey, B B D Sc, F I C, I E S, Professor of Chemistry, Presidency College, Madras

47 Dhar N R, D Sc, F I C, I E S, Deputy Director of Public Instruction, U P, Allahabad

48 Dhar, S C, M Sc, D Sc (Cal, Edin), F R S E., Professor and Head of the Department of Mathematics, Nagpur University, Nagpur (1938)

49 Dunn, J A, D Sc, D I C, F G S, Geologist, Geological Survey of India, Indian Museum, Calcutta. (1935)

50 Dunnicliff, H B, C I E, M A, Sc D, F I C, I E S, Chief Chemist, Central Revenues and Director, Control Laboratory, New Delhi

51 Dutt, S B, D Sc, D I C, Reader in Organic Chemistry, Allahabad University, Allahabad (1935)

52 Evans, P, B A, F G S, 156, Longlands Road, Sidcup, Kent

53 Fermor, Sir Lewis L, Kt, O B E, D Sc, A R S M, M Inst M M, F G S, F R A S B F R S, c/o Lloyds Bank, 6, Pall Mall, London, S W 1

54 Fowler, Gilbert J, D Sc, F I C, Consulting Chemist, Mackay's Gardens Annexe, Grames Road, Cathedral P O, Madras

55 Fox, C S, D Sc, M I Min.E, F G S, Director, Geological Survey of India, Indian Museum, Calcutta

56, Gee, E R, M A, F G S, Geologist, Geological Survey of India, Indian Museum, Calcutta, (1935).

57 GHOSE, S L, M Sc, Ph D, Professor of Botany, Government College, Lahore

58 GHOSH, J, M A, Ph D, Professor of Mathematics, Presidency College, Calcutta (1936)

59 GHOSH, J C, D Sc, Director Indian Institute of Science, Hebbal, Bangalore

60 GHOSH, P N, M A, Ph D, Sc D (Hon), F Inst P Ghosh Professor of Applied Physics, Calcutta University, 92, Upper Circular Road, Calcutta

61 GHOSH, R N, D Sc, Reader in Physics, Allahabad University, Allahabad (1939)

62 GLENNIE, LT COL E A, D S O, R E, Survey of India, Dehra Dun

63 GRAVELY, F H, D Sc, F R A S B, Superintendent, Government Museum, Museum House, Egmore, Madras

64 GUHA, B S, M A, Ph D, Assistant Superintendent, Zoological Survey of India, Indian Museum, Calcutta

65 GUHA, P C, D Sc, Acting Professor of Organic Chemistry, Indian Institute of Science, Hebbal, Bangalore (1935)

66 HADDOW J R, B Sc, M R C V S, D V S M, Veterinary Research Officer in charge of Serology, Imperial Veterinary Research Institute, Muktesar Kumaun, U P

67 HENDRY, D, M C, B Sc, N D A, Director, Imperial Chemical Industries, India, Calcutta (1938)

68 HERON, A M, D Sc, F G S, F R G S, F R S E, F R A S B, Mines and Geology Office, Hyderabad (Deccan)

69 HORA, S L, Rai Bahadur, D Sc, F R S E, F L S, F Z S, F R A S B, Asst Superintendent, Zoological Survey of India, Indian Museum, Calcutta

70 HUSAIN, M AFZAL, Khan Bahadur, M A, M Sc, I A S, Vice Chancellor, Panjab University, Lahore

71 IYENGAR M O P, M A, Ph D, F L S, University Professor of Botany, Madras University, Triplicane Madras

72 JOSHI, A C, D Sc, Assistant Professor of Botany, Benares Hindu University, Benares (1938)

73 KAPUR, S N, Ph D, Imperial Forest Research Institute, Dehra Dun

74 KICHLU, P K, D Sc, Professor of Physics, Government College, Lahore (1935)

75 KOSHY P K, F R C P, Professor of Anatomy, Medical College, Madras

76 KOTHARI, D S, M Sc, Ph D, Reader and Head of the Physics Department, Delhi University, Delhi (1936)

77 KRISHNA, S, Ph D, D Sc, F I C, Forest Biochemist, Imperial Forest Research Institute, Dehra Dun (U P)

78 KRISHNAN, K S, D Sc, Mahendra Lal Sircar Professor of Physics, Indian Association for the Cultivation of Science, 210, Bow Bazar Street, Calcutta

79 KRISHNAN, K V, M B B S, L R C P, D B, D Sc, Professor of Malariology and Rural Hygiene, All-India Institute of Hygiene and Public Health, Calcutta

80 KRISHNAN, M S, A R C S, Ph D, D I C, Geologist, Geological Survey of India, Indian Museum, Calcutta (1935)

81 LAL, R B, M B B S D P H, D T M & H, D B, Professor of Vital Statistics and Epidemiology, All India Institute of Hygiene and Public Health, Calcutta (1935)

82 LAW, S C, M A, B L, Ph D, M B O U, 50, Kailas Bose Street, Calcutta (1936)

83 LEWIS, BRIGADIER C G, O B E, Surveyor General of India, 13, Wood Street, Calcutta (1939)

84 MACMAHON, P S, M Sc, B Sc (Oxon), F I C, I E S, Professor of Chemistry, Lucknow University, Lucknow

85 MAHAJANI, G S, M.A, Ph D, Principal and Professor of Mathematics, Fergusson College, Poona 4

86 MAHALANOBIS, P C, M.A, B Sc, I E S, Professor of Physics, Presidency College, Calcutta

87 MAHESWARI, P, D.Sc, Reader in Botany, Dacca University, Ramna, Dacca (1935)

88 MATTHAI, GEORGE, M.A, Sc D, F L S, F Z S, F R S E, Professor of Zoology, Government College, Lahore

89 MEHRA, H R, M Sc, Ph D, Reader in Zoology, Allahabad University, Allahabad

90. MEHTA, K C., Rai Bahadur, M Sc, Ph.D, Professor of Botany, Agra College, Agra

91 **MILLS**, J P, M A, I C S, Secretary to H E the Governor, Government House, Shillong, Assam (1936)

92 **MITRA**, S K, M B E, D Sc, Ghose Professor of Physics, Calcutta University, 92, Upper Circular Road, Calcutta

93 **MITTER** P C M A, Ph D, Palit Professor of Chemistry, Calcutta University, 92, Upper Circular Road, Calcutta

94 **MOOKERJEE**, H K, D Sc, D I C University Professor of Zoology and Head of the Department Calcutta University 35, Ballygunge Circular Road, Calcutta (1939)

95 **MOWDAWALLA**, F N M A, M I E E, Mem A I E E, M I E, 301, Frere Road, Fort, Bombay

96 **MUKHERJEE**, J N, D Sc F C S, F R A S B Ghose Professor of Chemistry, Calcutta University, 92, Upper Circular Road, Calcutta

97 **NAIK**, K G, D Sc, F I C, Professor of Chemistry, Baroda College, Baroda

98 **NARLIKAR** V V B Sc (Bom) B A (Cantab), F R A S Professor of Mathematics and Head of the Department, Benares Hindu University, Benares (1939)

99 **NEOGI**, P, M A, Ph D, I E S (Retd), 44A, New Shambazar Street, Calcutta (1936)

100 **NORMAND** C W B M A, D Sc, Director General of Observatories, Meteorological Office Poona 5

101 **OLVER**, Col Sir Arthur, C B, C M G, F R C V S, Principal, Royal Veterinary College Edinburgh

102 **PANDIT**, C G, M B B S, Ph D, D P H, D T M, Offg Director, King Institute of Preventive Medicine, Guindy Madras (1939)

103 **PARANJPE**, G R, M Sc, A I I Sc, I E S, Principal and Professor of Physics, Royal Institute of Science, Bombay (1937)

104 **PARANJPYE**, R P, D Sc, Fergusson College Road, Poona 4

105 **PARIJA**, P K, M A, B Sc I E S Principal and Professor of Botany, Ravenshaw College, Cuttack

106 **PARKINSON**, C E, Deputy Conservator of Forests, Minbu Division Minbu, Burma (1936)

107 **PASRICHA**, Major C L, I M S, Professor of Pathology and Bacteriology, School of Tropical Medicine, Calcutta (1939)

108 **PERCIVAL**, F G, Ph D F G S, Superintendent of Mines and Quarries, Tata Iron & Steel Co, Ltd, 3, Beldih Lake Road, Jamshedpur (1936)

109 **PHILPOT**, H P, B Sc (Eng), A M Inst C E, M I Mech E, M I A E, M I M, Principal and Jodhpur Hardinge Professor of Technology, Engineering College, Benares Hindu University Benares

110 **PINFOLD**, E S, M A, F G S, Geologist, The Attock Oil Co, Ltd, Rawalpindi

111 **PRASAD**, B N, M Sc, D Sc, Ph D, Mathematics Department, Allahabad University, Allahabad (1936)

112 **PRASAD**, Mata, D Sc, F I C, Professor of Inorganic and Physical Chemistry, Royal Institute of Science, Bombay (1935)

113 **PRASHAD**, Baini, D Sc, F R S E, F L S, F Z S, F R A S B, Director, Zoological Survey of India, Indian Museum, Calcutta

114 **PRUTHI**, H S, M Sc, Ph D, Imperial Entomologist, Imperial Institute of Agricultural Research, New Delhi

115 **QURESHI**, Muzafaruddin, Ph D, Professor of Chemistry, Osmania University, Hyderabad (Deccan)

116 **RAJ**, B Sundara, Dewan Bahadur, M A, Ph D, Director of Fisheries, Madras (1935)

117 **RAMANATHAN**, K R, M A, D Sc, Meteorologist, Meteorological Office, Poona 5

118 **RAMDAS**, L A, M A, Ph D, Agricultural Meteorologist, Poona 5 (1935)

119 **RANGASWAMI AYYANGAR**, G N, Rao Bahadur, B.A, I A S, Millets Specialist, Agricultural College and Research Institute, P O Lawley Road, Coimbatore, S I.

120 **RAO**, B Rama, M A, D I C, F G S, Director, Geological Survey Department, Mysore State, Bangalore

121. **RAO**, L Rama, M A., F G S, Professor of Geology, Central College, Bangalore. (1939).

16 Prof J Perrin, N L, Sorbonne, Paris

17 Prof Robert Robinson, D Sc, F R S, Waynflete Professor of Organic Chemistry in the Dyson Perrins Laboratory, Oxford University

18 Sir E John Russell, D Sc, F R S, Director, Rothamsted Agricultural Experimental Station, Harpenden, Herts, England

19 Sir Albert C Seward, D Sc, Hon LL D, F R S, Formerly Master of Downing College and Emeritus Professor of Botany in the University of Cambridge, 209 Cromwell Road, London, S W 5

20 Sir Charles S Sherrington, O M, G B E, N L, F R S, Formerly Waynflete Professor of Physiology in the University of Oxford, Broomside, Valley Road, Ipswich, England

21 Dr C M Wenyon, C M G, C B E, F R S, Director-in chief, Wellcome Bureau of Scientific Research, 183, Euston Road, London, N W 1

APPENDIX II

ABSTRACT PROCEEDINGS OF THE COUNCIL, 1939

[Note —These abstracts of the proceedings of the Council relate to questions dealt with which are likely to be of interest to Fellows Routine matters and matters which are under consideration are not included]

1 The Council resolved that in future all arrangements regarding scientific programme of discussions or symposia arranged by the National Institute be made by a committee appointed by the Council for the purpose, consisting of the covener and two or three other members The committee shall be responsible for arranging the matter for publication and sending it to the editor in a form ready for the press within one month of the symposium being held In view of the large cost of publication it is suggested that only important contributions to the discussion should be published in full (No 8—8 2 39)

2 The following resolution passed at an emergency meeting of the Council was forwarded to the Private Secretary to His Excellency the Viceroy

'The President and Council of the National Institute of Sciences of India, on behalf of the Institute, loyally place their expert scientific knowledge at the disposal of the Government in the present crisis' (5 9 39)

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APPENDIX III.

COMMITTEES, 1940

SECTIONAL COMMITTEES

(1) 'Mathematics' Committee for Mathematics, Astronomy and Geodesy —

	To serve until Dec 31
Principal G S Mahajani	1940
Principal B M Sen (Secretary and Convener)	1940
Prof A C Banerji	1941
Prof M. R Siddiqi	1941
Mr T. P Bhaskara Shastri	1942
Brigadier C G. Lewis	1942

(2) 'Physics' Committee for Physics and Meteorology —

	To serve until Dec 31.
Dr D S Kothari	1940
Prof S K Mitra	1940.
Dr K R Ramanathan	1941
Prof M N Saha	1941
Dr K S Krishnan (Secretary and Convener)	1942
Prof S N Bose	1942

(3) 'Chemistry' Committee for Pure and Applied Chemistry —

Prof B B Dey	1940
Prof J C Ghosh	1940
Dr H K Sen	1941
Rao Bahadur B Viswanath	1941
Prof P C Mitter (Secretary and Convener)	1942
Dr S S Bhatnagar	1942

(4) 'Engineering Sciences' Committee for Engineering, Metallurgy, Electro technics and kindred subjects —

Dr G J Fowler	1940
Dr E Spencer	1940
Dr N K Bose (Secretary and Convener)	1941
Mr D Hendry	1941
Mr F N Mowdawalla	1942
Dr P N Ghosh	1942

(5) 'Geology' Committee for Geology, Palæontology, Mineralogy and Geography —

Dr M S Krishnan	1940
Dr F G Percival	1940
Dr A L Coulson (Secretary and Convener)	1941
Dr C S Fox	1941
Prof L Rama Rao	1942
Prof B Sahni	1942

(6) 'Botany' Committee for Pure and Applied Botany, Forestry and Agronomy —

Dr S L Ghose	1940
Prof S P Agharkar (Secretary and Convener)	1940
Prof B Sahni	1941
Rao Bahadur T S Venkataraman	1941
Dr K Bagchee	1942
Dr P Maheswari	1942

(7) 'Zoology' Committee for Pure and Applied Zoology and Anthropology including Ethnology —

Prof G Matthai	1940
Dr B Sundara Raj	1940
Dr C F C Beeson	1941
Rai Bahadur S C Roy	1941
Mr J P Mills	1942
Dr B Prashad (Secretary and Convener)	1942

(8) 'Physiology' Committee for Animal Physiology, Pathology, Bacteriology, Psychology and other Medical and Veterinary subjects —

Dr A C Ukil	1940
Lt.-Col H E Shortt	1940.
Lt Col S S Sokhey	1940
Col R Row	1941
Dr G Bose	1941
Mr. J R Haddow	1941.
Bt.-Col R N Chopra	1942
Dr C G Pandit	1942
Major C L. Pasricha (Secretary and Convener)	1942.

APPENDIX IV.

LIST OF INSTITUTIONS ON THE EXCHANGE LIST.

Indian

Allahabad

1 Allahabad University
2 National Academy of Sciences, India

Bangalore

3 Department of Agriculture, Mysore State
4 Electrical Engineering Society
5 Geological Survey Department, Mysore State
6 Indian Academy of Sciences
7 Indian Institute of Science
8 Meteorological Department, Mysore State
9 Society of Biological Chemists, India

Benares

10 Indian Botanical Society

Bombay

11 Anthropological Society of Bombay
12 Bombay Natural History Society
13 Indian Central Cotton Committee
14 Royal Institute of Science

Calcutta

15 Anthropological Society of India
16 Biochemical Society of India
17 Botanical Survey of India
18 Calcutta Mathematical Society
19 Calcutta Medical Club
20 Calcutta School of Tropical Medicine
21 Calcutta University
22 Carmichael Medical College
23 Geological, Mining and Metallurgical Society of India
24 Geological Survey of India
25 Indian Association for the Cultivation of Science
26 Indian Chemical Society
27 Indian Medical Gazette—(Thacker, Spink & Co. (1933), Ltd.)
28 Indian Physical Society
29 Indian Psychological Association
30 Indian Statistical Institute
31 Indian Tea Association
32 Institution of Chemists, India
33 Mining, Geological and Metallurgical Institute of India
34 Physiological Society of India
35 Royal Agri Horticultural Society of India
36 Royal Asiatic Society of Bengal
37 Science and Culture
38 Survey of India.
39 Zoological Survey of India

Coonoor

40 Pasteur Institute of Southern India

Dacca.

41 Dacca University

Dehra Dun

42 Board of Management, Indian Forester
43 Imperial Forest Research Institute

Hyderabad (Deccan)

44 Department of Mines and Geological Survey, H E H Nizam's Government
45 Osmania University

Indore

46 Institute of Plant Industry

Kasauli

47 Central Research Institute
48 Indian Journal of Medical Research
49 Malaria Institute of India

Lahore

50 Punjab University

Lucknow

51 Indian Zoological Memoirs
52 Lucknow University

Madras

53 King Institute of Preventive Medicine
54 Madras Fisheries Department
55 Madras Government Museum

Muktesar

56 Imperial Veterinary Research Institute

Naggar (Punjab)

57 Himalayan Research Institute, Roerich Museum

New Delhi

58 Imperial Council of Agricultural Research

Poona

59 Indian Mathematical Society
60 India Meteorological Department

Ranchi

61 Indian Lac Research Institute

Simla

62 Himalayan Club

Foreign

Canada

63 Department of Mines, Ottawa
64 Geological Survey of Canada, Ottawa

Cape Colony

65 South African Library, Cape Town

China.

66. Chinese Physical Society, Kunming.
67. National Agricultural Research Bureau, Nanking.

France.

68. Museum Natural d'Histoire Naturelle, Paris.

Germany

69 Chemisches Zentralblatt, Berlin

Great Britain

70 British Museum, Natural History Section, London
71 Imperial Bureau of Plant Genetics (for crops other than Herbage), Cambridge
72 Imperial Bureau of Plant Genetics (Herbage plants), Aberystwyth
73 Nature, London
74 Patent Office, London
75 Royal Botanic Gardens, Edinburgh
76 Royal Society of Edinburgh
77 Science Museum, London

Italy

78 Institut International d'Agriculture, Rome

Java

79 Departement van Economische Zaken, Batavia

Philippines

80 Philippine Bureau of Science, Manila

Russia

81 All-Union Lenin Library, Moscow

Uganda

82 Geological Survey of Uganda

U S A

83 American Chemical Society, Columbus
84 American Museum of Natural History, New York
85 Marine Biological Laboratory, Woods Hole, Mass
86 Scripta Mathematica, New York
87 Smithsonian Institution, Washington
88 Treasury Department, U S Public Health Service, Washington
89 U S Department of Agriculture, Washington
90 U S National Bureau of Standards, Washington
91 U S National Museum, Washington

APPENDIX V

LIST OF PERIODICALS RECEIVED IN EXCHANGE OR AS PRESENTATION

Indian

Agriculture and Livestock in India
Annual Report of the Calcutta School of Tropical Medicine
Annual Report of the Institute of Chemists, India
Annual Report of the Indian Tea Association
Annual Report of the Indian Central Cotton Committee
Annual Report of the Department of Agriculture, Mysore
Annual Report of the Indian Association for the Cultivation of Science
Annual Review of Biochemical and Allied Research in India
Astrographic Catalogue, Hyderabad Section.

Bulletin of the Indian Central Cotton Committee.
Bulletin of the Calcutta Mathematical Society
Bulletin of the Geological, Mining and Metallurgical Society of India
Bulletin of the Madras Government Museum
Bulletin of the Mysore Coffee Experiment Station
Calcutta Medical Journal
Electro technics
Geodetic Report of the Survey of India
General Report of the Survey of India
General Report on Village or Extra factory Consumption of Cotton in India
Health Bulletin (Malaria Institute of India)
Indian Forest Records
Indian Forester
Indian Journal of Agricultural Science
Indian Journal of Physics
Indian Journal of Medical Research
Indian Journal of Veterinary Science and Animal Husbandry
Indian Medical Gazette
Indian Medical Research Memoirs
Indian Zoological Memoirs
Journal of the Department of Science, Calcutta University
Journal of the Indian Chemical Society
Journal of the Indian Institute of Science, Bangalore
Journal of the Indian Mathematical Society
Journal of the Indian Medical Association
Journal of the Malaria Institute, India
Journal of the University of Bombay
Journal Osmania University
Journal of the Hyderabad Geological Survey
Magnetic, Meteorological, Atmospheric, Electrical and Seismological Observations made at the Government Observatory, Bombay and Alibagh
Memoirs of the Geological Survey of India
Memoirs of the India Meteorological Department
Memorandum, Indian Tea Association
Mysore Agricultural Calendar
Proceedings of the Institute of Chemists, India
Proceedings of the Indian Academy of Sciences, Bangalore
Proceedings of the National Academy of Sciences, India
Proceedings of the Society of Biological Chemists
Quarterly Journal of the Indian Institute of Science
Quarterly Journal of the Geological, Mining and Metallurgical Society of India
Records of the Geological Society of India
Report of the Institute of Plant Industry, Indore
Report of the Botanical Survey of India
Report of the Haffkine Institute, Bombay
Report of the King Institute of Preventive Medicine, Madras
Report of the Madras Fisheries Department
Science and Culture
Seismological Bulletin of the India Meteorological Department.
Scientific Notes of the India Meteorological Department
Siam Scientific Bulletin
Statistical Leaflets of the Indian Central Cotton Committee
Summary Proceedings of the Meetings of the Indian Central Cotton Committee
The Mathematics Student
Transactions of the Mining, Geological and Metallurgical Institute of India
Transactions Calcutta Medical College Re Union.

Foreign

American Museum Novitates, New York
Annals Jardin Botanique, Buitenzorg
Annual Report of the Geological Survey Department of Uganda
Biennial Report of Insect Control Work conducted by the National Agricultural Research Bureau, Chunking
Biological Bulletin of the Marine Biological Laboratory, Woods Hole, Mass , U S A.
Berichte der Deutschen Chemischen Gesellschaft, Berlin.

Bulletin of the Canada Department of Mines
Bulletin of the Geological Survey of Uganda
Bulletin of the National Museum of Canada
Bulletin (Herbage Publication Series), Imperial Bureau of Plant Genetics, Aberystwyth
Bulletin of the U S National Museum, Washington
Collected Reprints of the Woods Hole Oceanographic Institute
Contributions from the U S Herbarium, Washington
Crop Reports of the National Agricultural Research Institute, Nanking
Experiment Station Record, U S Department of Agriculture, Washington
Himalayan Journal
International Revue of Agriculture, Rome
Journal of the American Chemical Society
Journal Sanghai Institute of Science
Memoirs of the Canada Department of Mines
Notes from the Royal Botanic Gardens, Edinburgh
Proceedings of the Royal Society of Edinburgh
Proceedings of the U S National Museum
Papers in Physical Oceanography and Meteorology, Woods Hole Oceanographic Institute
Report of the National Research Council, Washington.
Report of the National Agricultural Research Bureau, Chungking
Report of the Canada Department of Mines
Scripta Mathematica, New York
Technical News Bulletin of the National Bureau of Standards, Washington
Transactions and Proceedings of the Botanical Society of Edinburgh
Treubia

APPENDIX VI

THE NATIONAL INSTITUTE OF SCIENCES OF INDIA

Receipts and Payments Account for the year ended 30th November, 1939

RECEIPTS	Rs	A	P	Rs	A	P
To Balance brought forward				47,194	13	3
,, Members' Admission Fees				256	0	0
,, Members' Subscriptions				5,714	2	0
,, Contributions towards publication of 'Indian Science Abstracts'				600	0	0
,, Sale of Authors' extra copies and Publications				457	12	9
,, Sale of 'Indian Science Abstracts'				242	8	0
,, Interest on Investments				1,347	6	7
,, Grants-in-aid—						
Government of India	6,000	0	0			
Universities	700	0	0			
				6,700	0	0
,, Refund of Advance				9	0	0
,, Collections for Lunch				330	0	0
,, Miscellaneous Receipts				33	6	0
TOTAL . ..				62,885	0	7

PAYMENTS	Rs	A	P	Rs	A	P	Rs	A	P
By Salaries of Staff							2,920	8	0
,, Printing Circulars, Notices, etc							145	8	0
,, Printing Publications, Reports, etc							5,651	12	3
,, Printing 'Indian Science Abstracts'							4,549	0	6
,, Contributions to other Science Academies under Rule 19							1,128	0	0
,, Honoraria, etc for preparing abstracts for 'Indian Science Abstracts'							1,376	13	0
,, Postage							561	3	6
,, Stationery							143	14	6
,, Office Equipment							115	0	0
,, Audit Fee							50	0	0
,, Travelling							158	9	6
,, Rent of Office							600	0	0
,, Advances to Staff							17	0	0
,, Expenses for Lunch							288	14	0
,, Miscellaneous Expenses							113	13	3
,, Bank Charges							19	9	0
,, Cash and Other Balances—									
Investments—	Rs								
3½% G P Notes 1842/43	5,000								
3½% ,, 1854/55	2,000								
3½% ,, 1865	6,000								
3½% ,, 1879	2,000								
3½% ,, 1900/01	8,000								
4% Loan 1960/70	17,000								
	40,000								
At cost				40,786	13	10			
With Imperial Bank of India—	Rs	A	P						
On Savings Bank Account	2,166	7	0						
On Current Account	2,079	5	3						
				4,245	12	3			
In hand				12	13	0			
							45,045	7	1
TOTAL							62,885	0	7

Examined with the Books and Vouchers and found in accordance therewith

PRICE, WATERHOUSE, PEAT & CO
Chartered Accountants,
Registered Accountants. } *Auditors*

CALCUTTA,
7th December, 1939.

APPENDIX VII.

BUDGET ESTIMATE FOR 1939-40

	1938 39 Estimate	1938 39 Actuals	Estimate for 1939-40
Ordinary Receipts			
Subscriptions	5,500	5,440	5,500
Interest	1,200	1,347	1,400
Contributions towards publication of 'Indian Science Abstracts'	500	600	500
Sale of Publications including 'Indian Science Abstracts'	300	700	500
Grants in aid	700	700	800
Grant in-aid from Government of India	6,000	6,000	6,000
Miscellaneous Receipts		33	
Contribution from General Fund	2,450	2,713	4,050
	16,650	17,533	18,750
Extraordinary Receipts			
Admission Fees	320	256	320
Compounding Fees		274	131
	320	530	451
Ordinary Payments			
Salaries and allowances	2,700	2,920	3,300
Publications including 'Indian Science Abstracts'	9,000	10,346	10,500
Contributions to co operating academies under Rule 19	1,200	1,128	1,200
Furniture	500	115	400
Postage	500	561	600
Stationery	150	144	150
Audit Fee	50	50	50
Honoraria, etc for preparing abstracts for 'Indian Science Abstracts'	1,200	1,377	1,300
Travelling	600	159	500
Office Rent	600	600	600
Miscellaneous	150	133	150
	16,650	17,533	18,750
Extraordinary Payments.			
Funding of Admission Fees and Compounding Fees	320	530	451

Annual Address to the National Institute of Sciences of India.

MADRAS, 1940

By BREVET-COLONEL R. N. CHOPRA, *C.I.E., M.D., Sc.D., F.R.C.P., I.M.S. (Retd.), Director, School of Tropical Medicine, Calcutta*

I. GENERAL

Annual Address

In the first Annual Address to the Institute, which was delivered at Indore in January 1936, Sir Lewis Fermor made a suggestion with regard to the type of address that the Presidents of the Institute should deliver annually. His suggestion was so judicious and practical that it was willingly adopted by his successors, and following this lead I also propose to preface the main part of my address with a brief review of the activities of the Institute during the past year of my office as its President. My immediate predecessor, Prof. Megh Nad Saha, F.R.S., during the two years of his office as President devoted so much time and thought to the work of the Institute that we were all very sorry when his term of office ended. I wish I could have devoted that much time to the work of the Institute, but unfortunately with my other duties, this has not been possible. I have, however, tried my best to keep up the tradition of my illustrious predecessors, and I hope that I have, at least, succeeded in directing and maintaining the policy of the Institute along the right lines.

Activities of the Institute

Since our last Annual Meeting at Lahore the affairs of the Institute have progressed in a satisfactory manner. It is a matter of congratulation that notwithstanding the stress of economic conditions our material prosperity has remained almost unabated during the last 12 months. It is true that we have received no fresh donations and that a number of our annual grants also have not been paid up, but we hope that this state of affairs is only temporary and that no serious repercussions resulting from the war in Europe will adversely influence our progress. The activities of the Institute have naturally been restricted to some extent by the prevailing abnormal conditions, but our record of the past year's activities, as detailed in the Annual Report, reflects great credit on the Council of the Institute and its administrative officers for the conduct of its affairs.

Fellows

The number of our Fellows at the beginning of the year was 157 Ordinary Fellows and 17 Honorary Fellows. Three Ordinary Fellows resigned and 11 Ordinary Fellows and 4 Honorary Fellows were elected during the year. The total number at present is 165 Ordinary

Fellows and 21 Honorary Fellows This number, considering the prevailing conditions in the country and the statutory limitations in regard to new elections, is satisfactory, but the Council will have to consider at an early date ways and means for extending the Fellowship if the activities of the Institute are to be maintained and extended

Meetings of the Institute

Our annual general meetings have followed the annual meetings of the Indian Science Congress Association ever since the first Meeting at Indore in 1936 The last Annual Meeting was held in the Hailey Hall, Lahore, on the 2nd of January, 1939 Owing to ill-health Prof Megh Nad Saha, the President for the year, unfortunately could not attend the meeting and his address had to be read by Dr S K Mitra A full account of the meeting was published in the *Proceedings* Two additional General Meetings were held during the year, one on the 5th of April and the second on the 25th and 26th of August, 1939 in the hall of the Royal Asiatic Society of Bengal An important symposium on 'Coal in India' was organized for the second meeting by Dr C S Fox, Director, Geological Survey of India, on behalf of the Institute The symposium embraced all significant aspects of the important problem of the main fuel resource of this country and it is hoped that the papers which were presented during the symposium and the discussions which followed on them will lead to results of practical importance to the country A detailed account of this symposium and of the papers read will, it is expected, be published in our *Proceedings* at an early date I am glad to be able to say in this connection that as a result of the discussions during this symposium an important resolution urging the necessity for the formation of a Fuel Research Board in India was passed by the Institute This resolution has been forwarded to the Government of India for their consideration, and it is hoped that it will result in some practical steps being taken for the formation of a Fuel Research Board and the protection of the highly important coal industry of the country

Resolution on War

The Council held seven Monthly Meetings for the transaction of ordinary business and an emergency meeting on the 5th of September 1939, soon after the outbreak of the war in Europe, at which the following resolution was passed

'The President and Council of the National Institute of Sciences of India, on behalf of the Institute, loyally place their expert scientific knowledge at the disposal of the Government in the present crisis '

This resolution was communicated to the Private Secretary to His Excellency the Viceroy, and I am sure all the Fellows of the Institute will be glad to render such expert services as they possibly can during the present crisis

Science and Social Relations

A committee was appointed during the year to consider the replies received in connection with the questionnaire on Science and its social relations—a work which the Institute had undertaken to do on behalf of the Government of India It is hoped that the committee will soon be able to report and suggest the necessary action that should be taken in the matter

Publications

The publication of our *Proceedings* and *Transactions* has been continued, three numbers of the former and two of the latter having been issued during the year The work in connection with our third publication the *Indian Science Abstracts* is particularly arduous, and our General Editor, Dr Baini Prashad, deserves our gratitude for the able and expeditious manner in which the publications of the Institute have been brought out He has on several occasions explained the difficulties in the matter of prompt publication of the abstracts of literature for any particular year, in spite of sustained efforts only 3 parts of the *Abstracts* for 1936 and 1937 could be published during the year It may also be mentioned that this work is very expensive, and though the Council of the Institute is grateful for the grants-in-aid received and the co-operation of the associate editors and various other bodies who have helped in this connection, the continuation and publication of this work within a reasonable time will depend on more funds being available and the active support of all scientists and scientific bodies throughout the country The work in connection with this publication is becoming more and more heavy, and we cannot possibly expect Dr Prashad to give us any more time than he is already devoting to this difficult task It will eventually mean the appointment of a paid Assistant Editor, but unfortunately our financial resources at present do not allow of any more staff We hope, however, that things will improve and this important activity of the Institute will continue to flourish

Quinquennial review

Sir Lewis Fermor in discussing the programme of work of the Institute in 1935 announced that the Council proposed 'to resuscitate in a different form the labours of the Board of Scientific Advice by publishing annually a review of the progress of Science in India' Owing to the very onerous nature of the task and the inherent difficulties in its execution, it has not been possible to issue such a review up till now, and it is very doubtful whether with our present resources we will ever be able to issue such a work every year Fortunately for us very detailed reviews of the progress of Science in India in all its branches by various authorities up to the end of 1937, with an excellent summary by the editor, Dr Baini Prashad, were included in that monumental publication of the Indian Science Congress Association—'The Progress of Science in India during the past twenty-five years'. I have carefully considered this question during the past year, and while inviting the views of the Fellows of the Institute, suggest that instead of an Annual review we may plan a Quinquennial review, and the first issue should deal with the period 1938–42 If this view commends itself to the scientists all over the country, we will have to start getting together the material immediately so as to have the work ready for issue in 1943.

Finance

I have already referred to the question of finances of the Institute As detailed in the Annual Report, we have received a number of annual grants from the Government of India, various Universities and other bodies, but the grants are not nearly sufficient for the work which the Institute has to carry out Unfortunately it has not been possible to get any grants from any of the Provincial Governments so far, and I would again appeal to all of them for generous financial support, which alone would enable the Institute to perform all its functions efficiently

Objects of the Institute

Our Institute was founded to fill an urgent need so keenly felt by scientific workers all over India for a body which could co-ordinate the work of various scientific societies, institutions and Government scientific departments and services throughout the country With this end in view the Organizing Committee of the Institute wisely laid down the first five main items of its programme as follows —

(a) The promotion of natural knowledge in India including its practical application to problems of national welfare

(b) To effect co-ordination between scientific academies, societies, institutions, and Government scientific departments and services

(c) To act as a body of scientists of eminence for the promotion and safeguarding of the interests of scientists in India and to represent internationally the scientific work of India

(d) To act through properly constituted National Committees in which other academies and societies will be associated, as the National Research Council of India, for undertaking such scientific work of national and international importance as the Council may be called upon to perform by the public and by Government

(e) To publish such proceedings, journals, memoirs and transactions, and other publications as may be found desirable

Since its foundation in 1935 the Council of the Institute has left no stone unturned to further this programme, but financial and other difficulties have been a serious hindrance in the full performance of some of its activities. The publications and meetings of the Institute have been arranged with a view to bringing to the notice of the authorities and the general public the very important and pressing question of exploring and developing the material wealth of this vast sub-continent and for harnessing the scientific resources for their proper exploitation Pious resolutions alone, however, cannot supplant active measures which are essential for developments of the type indicated above.

Resources of India

India has fortunately been richly endowed by nature with all that any country can possibly need While primarily an agricultural country, with extensive agricultural and forest lands capable of yielding almost all kinds of foodstuffs, timber and other economic products, it also has very rich resources of various minerals on which depends the highly industrialized life of the present times Its power resources in the way of coal and water power are also very extensive, but have not been adequately developed According to Sir M Visvesvarayya only 2% of the Hydroelectric resources of India have so far been developed In those respects India can rightly be designated as one of a triumvirate with the United States of America and the Russian Socialist Federated Soviet Republic, the only two other countries of the world which have almost unlimited agricultural, mineral and power resources As compared to the other two units of this triumvirate, however, those resources in India have for want of a systematic policy of industrialization not been developed, and naturally, therefore, India stands very low in the list of industrialized countries of the present day This unfortunate position of India is intimately connected with the organization and development of scientific and technical education and research in the country and the lack of an industrial policy A very serious situation has suddenly arisen as a result of the war which Germany has forced on the world and the repercussions of which are already materially influencing life in every country Its direct effects on India are already becoming a source of great concern both for the authorities and the public at large, as we are dependent for the great majority of manufactured commodities on imports from foreign countries This has been brought home to me very forcibly in connection with the drug industry, which seemed to be apparently making a headway, but the outbreak of war has brought to the fore the very serious problem of the supply of the basic materials for the manufacture of medicinal preparations practically all of which were being imported from foreign countries This is a situation which no self-respecting country should face with equanimity It would not, therefore, be out of place if I may briefly review the situation to-day and indicate the urgent necessity for the proper planning and organization of scientific research as this alone will make it possible for India to assume its proper place in the comity of nations, and be as independent as possible of imports from other countries of even the daily necessities of life

Progress of scientific education and research

Sir Lewis Fermor and Dr Baini Prashad have within recent years discussed the organization and progress of scientific education and research in India, and the late Lord Rutherford also included a brief review in his Presidential Address to the joint session of the British Association for the Advancement of Science and the Indian Science Congress Association in 1938 It would, therefore, suffice if I include only a very brief summary here

Education on Western lines was introduced into India within comparatively recent times and it is, therefore, remarkable that its progress in the country has been so rapid The first universities in this country were founded at Calcutta, Bombay and Madras in 1857, but these and others founded in the latter half of the 19th century were only universities of an affiliating type and their energies were mainly directed towards examining students for various examinations and degrees, rather than serving as centres of teaching or research With the passing of the University Act of 1904, however, most of the universities instituted courses for advanced studies and special Honours courses in scientific subjects and, by the appointment of professors and lecturers and the extension of libraries and laboratories, materially advanced the cause of scientific teaching and original research in the country A start had been made in regard to scientific education in the latter half of the 19th century, but this teaching was mainly confined to preliminary studies rather than more advanced teaching or research The major part of advances to our knowledge in the scientific sphere in India up to the beginning of the 20th century was due to the scientific departments of the Government and work of independent workers who devoted their spare time and energies to studies in subjects which interested them In a number of cases such devotion to research was looked down upon, and I cannot do better than cite the classical example of Sir Ronald Ross who was actually rebuked for devoting all his spare time to the study of mosquitoes, this incidently resulted in the discovery of the very important rôle played by mosquitoes in the spread of Malaria

University education since this period has progressed at a remarkably rapid rate, but the reorganization of the secondary school system to guarantee a sound basic education and primary scientific training, and the reorganization of the University studies with a view to ensuring a sound knowledge of the fundamental sciences to serve as a foundation for advanced study and research are still urgent desiderata

Necessity for development of research activities

In the recently reorganized teaching universities in addition to their capacity for imparting training in various scientific subjects, research qualifications in the case of the professors and lecturers were rightly regarded as requisites for appointment and promotion, but Prof Saha rightly pointed out the defects of the present-day situation when he remarked that 'owing to intrigues by vested interests, and defects in the constitution, these ideals are being lost sight of, nay even abandoned in many of the universities, and some of them are being reconverted to the high school stage from which they were rescued by the reforms of 1921-22'

After the World War of 1914–18 greater attention was paid to the re-organization, on a more extensive basis, of the various Government scientific departments and research institutions, and a number of special research institutions were founded Unfortunately the Board of Scientific Advice, which the Government of India had established in 1902 for the co-ordination of scientific work carried out by its official agencies, was closed down in 1924, and though proposals for the foundation of a National Research Council to replace this Board have been under consideration for several years, the scheme has not hitherto materialized The Indian Research Fund Association which was founded in 1911 for the prosecution and assistance of research in connection with the causation, mode of spread and prevention of diseases in India has been carrying on a very useful work, but for want of funds its activities have been greatly restricted since 1931 The Imperial Council of Agricultural Research constituted in 1929 and the Indian Central Cotton Committee and the Indian Central Jute Committee, have done very valuable service in arranging agricultural, technological and economic research in connection with agriculture, in effecting the improvement of various types of crops, and in studying the factors connected with the marketing of the products, but even here lack of funds has been a serious hindrance in the way of progress Though a number of official organizations exist for the development of Medical and Agricultural Research, there are no institutions worth the name for the advancement of Industrial Research Various private bequests resulting in the Indian Association for the Cultivation of Science, Calcutta, the Tata bequest resulting in the foundation of the Indian Institute of Science at Bangalore, Sir Tarak Nath Palit, Sir Rash Behary Ghosh and Khaira bequests leading to the establishment of the University College of Science at Calcutta, the Bose Research Institute, Calcutta, founded and endowed by Sir Jagadish Bose, Rai Bahadur Lakshminarain bequest to the University of Nagpur, the Maharaja of Jeypore bequest leading to the foundation of the Science Departments of the Andhra University, contributions from the Rockefeller Foundation towards the All-India Institute of Hygiene and Public Health and the Attock Oil Company bequests to the Punjab University are responsible for the creation of a number of important agencies for the advancement of higher teaching and research in various sciences With all those, however, the facilities for teaching and research in various sciences in the vast sub-continent of India have been and still are very limited, and it is, therefore, a matter of real pride that in spite of these handicaps Indian students of science have, during this short period of a little over a quarter of a century, justified their capacity for original investigation In the words of the late Lord Rutherford 'India is now taking an honourable part and an ever increasing share in the advance of knowledge in pure science' As Prof Saha, however, very cogently pointed out, 'the time has now come not only to strengthen the scientific surveys and the research atmosphere of the universities, but we ought to enter on a third phase, namely, scientific research should now be applied for solving the industrial problems of the country'

Value of Industrial Research

Lord Rutherford in his Presidential Address, already referred to, gave a very valuable summary of the organization of industrial research in Great Britain, and, though great differences exist between agricultural and industrial conditions in Great Britain and India, it would be of value to give here a brief summary of how the British Government have contributed to the promotion and organization of industrial and agricultural research in the period since the World War of 1914–18

Prior to the World War progress in industry 'depended, in the main, on the brilliant contributions of individual workers, rather than on any systematic attack by scientific methods on the problems of industry' The World War, however, brought the industrialists and the men of science into closer contact to their mutual benefit The Government also recognized that a more systematic application of science and research over a broader field was essential in the national interest, and in 1915 a special Department of Scientific and Industrial Research was founded This was followed by the Medical Research Council in 1920 and the Agricultural Research Council in 1931 In fact the establishment of the Department of Scientific and Industrial Research marked the first organized measure taken in Great Britain for helping industry through the application of science Several new organizations controlled and financed by this Department were set up to deal with the scientific aspects of the use of fuel, of the storage and transport of food, of buildings, roads, etc, and the famous National Physical and the Chemical Research Laboratories at Teddington were developed under the aegis of this Department As a result very important national organizations have been built up for the investigation and application of science to various problems connected with the daily life of the people and the nation's industry as a whole 'In the British organizations there is no political atmosphere, but of course the responsibility for allocating the necessary funds ultimately rests with the Government' The planning of the programmes of research, however, 'rests with research councils or committees who are not themselves State servants but distinguished representatives of pure science and industry', this work being mainly in the hands of the Advisory Council of the Department of Scientific and Industrial Research Similar research organizations under the control of Research Councils or corresponding bodies, which have been set up in Canada, Australia, New Zealand and South Africa, are responsible for the rapid scientific and industrial developments in these dominions

The late Lord Rutherford in discussing the development of industrial research in Great Britain remarked

National Research Council for India

'Even in a large country like India, where the resources and needs of the different Provinces are very varied, it seems to me essential for efficiency that the organization of research should be on national rather than on provincial lines The setting up of separate research establishments for similar purposes in the various provinces cannot but lead to much overlapping of work and waste of effort and money Such a central organization of research does not necessarily mean that the scientific work should all be concentrated in a single laboratory' If research work is to be of real and lasting value it must be carried out in the interests of the country as a whole and not of any particular province or area As was well summed up in a leader in *Nature*, 'This necessitates careful planning and co-ordination of various schemes for research in all branches of science, whether pure or applied In formulating the future policy, India should profit by the experience of Canada and Australia where the working of the scientific departments of the State or Provincial Governments *vis-à-vis* those of the Central or Federal Government has shown that the research organizations of the country should be truly national and responsible to the Federal Government alone The detailed planning of research must be in the hands of those with the necessary specialized knowledge, and they must be able to act without suspicion of political or racial influence ' In other words, a plea is made for the foundation of a National Research Council in India on the lines of the body which ever since its constitution has been rendering such useful service in Great Britain The Council should not only define the policy but act as an expert advisory body for planning and co-ordinating all scientific research in the country The planning of scientific policy and co-ordination of research should be so arranged as to preclude duplication and avoid wastage of talent and available funds, but without in any way restricting the normal work of the universities, scientific departments and institutions, or in any way curbing individual initiative which is always so essential for high class research Such an authoritative body should also be able to help in bringing about the necessary reforms in the existing system of scientific education The Council should be liberally endowed so as to be independent of annual appropriations for carrying out all its programme of work

Scientific and Industrial Research

Pure scientific research is as essential as that specifically devoted to the attainment of any industrial object While industrial research is confined specifically to investigations which have a direct bearing on the development of any industry, it would be a truism to assert that discoveries made in the domain of pure science may and often find application in industries at a later date, and that 'industrial application, though its precise form cannot always be foreseen at the time, has come to be an expected incident in the after-life of the discovery' This principle is fully accepted in the highly organized machinery for industrial research in the United States of America, and as a result a great deal of importance is attached to researches in pure sciences The connection of such researches with any of the industries is often not obvious, but all the same they are encouraged in the hope that they may provide the raw material for industrial research, and further owing to the interdependence of different investigations, progress in any one science may have a very marked bearing on the development of others Industrial research work in the United States of America, according to Flemming, has developed along certain definite stages.

(*a*) Industrial research applied to the elimination of manufacturing troubles

(*b*) Research having some new and specific commercial object.

(*c*) Research in pure science with no specific commercial application in view.

(*d*) Research applied to public service

(*e*) Research for the purpose of establishing standard methods of testing and standard specifications connected with the purchase of raw materials

Research laboratories in the States are attached to or supported by manufacturing corporations, associations of manufacturers, universities and colleges, national institutions, commercial laboratories and scientific societies

Apart from numerous endowments and appropriations made for research to various universities, colleges and Government departments, there are in the States a large number of funds that have been established for the endowment of scientific research alone Though a number of them are for the promotion of industrial research, others were founded for providing the necessary funds for medical, astronomical and general research in other sciences In 1917 a National Research Council was appointed by the National Academy of Sciences at the request of the President of the United States This Council includes the most prominent research men in the States and all departments of research are fully represented Its object is to co-ordinate the scientific research work of the country in order to secure efficiency in the solution of the problems of war and peace, and this Council has rendered possible the nationalization of research in the country Selection and training of research men have also been given special attention to, and it has been found that 'while full credit should be given to the genius who can often achieve so much with very limited facilities, it is a fallacy to assume that research work of great value cannot be carried out by men of more than average attainments This is illustrated by the success achieved in many of the laboratories in the States, where, with suitable organization, important investigations both directly connected with industry and in pure science have been successfully dealt with by men of no more than average ability working under competent direction'

Industry has rightly been styled as the basis of national prosperity, and it is, therefore, necessary that every resource should be used to facilitate its progress In this connection research is of the utmost importance and it must be regarded as an indispensable weapon with which to develop industries of any country and to cope with international competition

The National Planning Committee which has been working in Bombay for the past several months is collecting detailed data in regard to industrialization of the country in all its aspects and other national problems, and it is hoped that its work would prove valuable in laying down the lines for future development in the country

Concluding Remarks

I have given you a bird's-eye view of the organization and development of scientific research and studies in India up to the present day, and of the lines followed in Great Britain for the organization and development of scientific research, both pure and applied, the latter with particular reference to the needs of industry and the life of the people I have also incidentally referred to the development of similar machineries in Canada, Australia, New Zealand and South Africa, and, finally, to the highly organized system in the United States On the analogy of these great industrial countries, I give below the outlines of a scheme for developing a similar organization in India to plan and co-ordinate research so as to avoid wastage both of talent and funds, preclude duplication, employ the available scientific personnel to the best advantage, and, finally, to arrange for the training of a much larger number of research personnel to supply the needs of the developing industry

Starting from the top I consider it absolutely essential that there should be a separate department of the Central Government corresponding to the Department of Industrial and Scientific Research in Great Britain It should be staffed by scientists with administrative experience and not by civilian administrators, and this I consider to be the absolute *sine-qua-non* of the whole scheme Civilian administrators, though they are admirably suited to carry on the civil and military side of the Government, have unfortunately seldom realized the exact needs of Science in the country, and as a result the progress of Science in India has been materially slowed down, if not actually hindered The Department should have an Advisory Council, the National Research Council, constituted on the lines of the Research Councils of other countries for planning and co-ordinating research, to promote and develop not only scientific but industrial research in the country, and finally for devising ways and means to make India independent, so far as possible, of foreign imports by a well-planned survey and development of its economic resources It is only then that it would be possible for this country to assume its right place among the industrially developed countries of the world With a view to harnessing Science in the service of Industry, the proposed Department and its Advisory Council will also have to explore ways and means for extending the existing machinery of scientific education in the country, from the school to the university stage, develop applied scientific training and research, and finally to see that research, whether in pure or applied sciences, is undertaken with a definite end in view and not only as a means for self-glorification.

I have only given the broad outline of the scheme, as I am of the opinion that its details can only be evolved after careful consideration of the *pros* and *cons* by an expert committee on which all elements of science and industry in the country are fully represented Let us hope that this scheme will commend itself to the Government and that steps will be taken at a very early date to bring into being such an agency, this alone will enable the country to steer a safe course in the face of the Armageddon which is now threatening the world.

II INDIAN FLORA, ITS MEDICINAL AND TOXIC PROPERTIES

Medicinal and Poisonous Plants

I come now to the second part of my address For the past twenty years I have been interested in the Indian flora in connection with the medicinal and toxic properties of the different plants and I propose to present to you some of the aspects of this work which are of interest both from the scientific and economic points of view I have selected this subject as owing to the outbreak of the war, the question of the supply of medicinal drugs in this country has assumed considerable importance, and I feel that a review of this work may help at least towards a partial solution of this vital problem Further, the significance of the large numbers and wide prevalence of the plants toxic to man, livestock and insects has not so far been fully appreciated in this country, and I hope that this review will stimulate interest in this direction Vast as the vegetable resources of this country are, I am convinced that they are not being properly exploited to the best advantage of the people of this land

General considerations

Climate and topography

The extreme variability that India presents in its meteorological and climatic conditions as also in its topographical features is perhaps unrivalled in the world The tremendous range of variation of temperature from 126°F in summer at Jacobabad to —46°F in winter at Dras and the prevalence of arctic conditions throughout the year in some of the Himalayan ranges, rainfall from 430 inches at Cherrapunji in the hills of Assam to less than 5 inches per annum in the desert areas of Rajputana, saturation of air with moisture in the coastal districts and in the hills during the south-west monsoon to periods of practically zero relative humidity in the dry weather during the north-east monsoon, are some of the interesting contrasts presented by the country No less striking are its physical features It has the most massive and the loftiest range of mountains in the world, the Himalayas, there are also lower hills and plateaus, extensive rich alluvial plains, sandy wastes and deserts, hill streams, mighty rivers with their extensive deltaic and estuarine systems, numerous lakes, canals, ponds, tanks and extensive marshy tracts, sandy or rocky coasts spread over an area of 1,575,107 square miles It has in fact been described as an epitome of almost all climates, seasons, and soils of the British Empire Under these conditions it is not surprising that India has one of the richest and certainly the most varied flora of any area of similar size on the surface of the globe

Features of Indian Vegetation

Roughly speaking, one-fifth of the Indian Empire is occupied by forests of different kinds. There are evergreen forests occupying the west coast of the Peninsula up to the ridges of the western mountain chain, and the lower slopes of the Eastern Himalayas, with their magnificent and majestic trees, the 'sky scrapers', and the Carnatic evergreens characterized by the comparatively smaller size of their trees A large part of the Peninsula is covered by the deciduous type of forests which are very valuable to the country There are the dry forests of Rajputana and the Punjab which are also spread over a large area of Indian States, these become drier and drier towards the west and south-west and disappear into the deserts on both sides of the lower Indus, there being very little vegetation of any kind in the Great Indian Desert itself Many tidal creeks and backwaters along the coasts of India, chiefly the deltas of rivers, such as the Sundribans are covered with another type of evergreen forest, the tidal or littoral, where many plants send up from their underground roots a number of aerial roots for respiration The massive chain of the Himalayas with its tropical, temperate and alpine flora presents unique features The eastern Himalayan flora differs remarkably from the western in several respects in addition to the disappearance of the tropical type as the extreme north-west is reached It is in this chain that the highest limit of vegetable life on earth has been recorded The tree limit in the Western Himalayas corresponds roughly with the snow-line, *i e*, 12,000 ft above sea level, above which a variety of beautifully coloured flowers flourish Aquatic or semi-aquatic types of vegetation are found in the tanks, jhils, ponds, water-courses, and swamps all over India, particularly in Bengal Lastly, there are areas in the plains, as well as in the hills, especially in the former, which have, through the influence of man in search of more and more agriculturally exploitable land, lost much of their original characters Another feature of the Indian vegetation is that in one season of the year vast areas in the plains of India are the scene of plenty for man and animals, in another they become a dreary brown sunburnt waste where herbivores starve by the thousands and where it passes human understanding how any creature dependent on plant life can survive the dry season

Relationship to other floras

The Indian flora is closely related to that of some other countries, and it is interesting to remark that none of the families of flowering plants is peculiar to this country There is a very great preponderance of those genera and species which are also found in the adjacent countries Malayan, Burmese and Chinese genera are specially well represented in Eastern India Next in order come European and middle east floras which are particularly strongly represented in Western India, and of the typically European elements there are twice as many in the Western as in the Eastern Himalayas Nearly 600 European genera are represented in India, many of them by a single species, and the middle eastern element is certainly, as is to be expected, no less prominent African, Australian and American elements follow these in decreasing proportions, the African flora being more noticeable in Western India Recently there has been an influx of American species, with their remarkable tendency to spread Tibetan and Siberian floras only reach India in the alpine regions of the Himalayas, while Chinese and Japanese elements are strongly represented in its temperate belts

Medicinal Plants of India

General

India abounds in all kinds of food plants, spices, perfumes, timber, fibres, gums, etc, which have been known all over the world from ancient times There are more than about 700 important fodder plants including about 260 species of valuable fodder grasses It is not surprising, therefore, that plants containing active and medicinal principles also grow abundantly within its bounds More than 2,000 plants, out of a total of about 11,000 species found in India, are alleged to have medicinal properties of some description or other and have been enumerated in the literature of indigenous medicine Nearly three-fourths of the drugs mentioned in the British and other Pharmacopoeias grow here in a state of nature and others can be easily grown Indeed, this country is a veritable emporium of drugs The families to which the larger numbers of medicinal plants belong are Leguminosae, Compositae, Labiatae, Euphorbiaceae, Rubiaceae, Rosaceae, Gramineae, Liliaceae, Rutaceae, Ranunculaceae, Umbelliferae, Cucurbitaceae, Solanaceae, Apocynaceae and Malvaceae

It stands to reason that all these 2,000 odd plants cannot have the wonderful virtues attributed to them, but it is believed that there are some of these which might rightly deserve the reputation they have earned as cures It was to find out what these were that their study was first begun in the early part of the last century Although many workers including Jones, Ainslie, Roxburgh, O'Shaughnessy, Moodeen Sheriff, Dymock, Watt, Kirtikar and Basu and others carried out laborious investigations, the pharmacology of most of the indigenous remedies remained an unexplored field till recent years

Medicine is intimately related to chemistry and experimental work on the pharmacological side can only be carried out in laboratories properly equipped with modern appliances None of these were available in this country till the Calcutta School of Tropical Medicine was established in 1921 Then for the first time proper collaboration between chemists, botanists and pharmacologists was rendered possible, while arrangements for clinical trials of the drugs were made by the establishment of the Carmichael Hospital for Tropical Diseases Work on medicinal plants was thus started by my colleagues and myself and our first main objective was to make India self-supporting by enabling her to utilize drugs produced in the country and by manufacturing them in a form suitable for administration There are a number of drugs of established therapeutic value which are in use in the pharmacopoeias of different countries The majority of these grow wild in great profusion in many parts of India and a certain number are even cultivated If these resources could be utilized and the finished products manufactured, treatment of many diseases could be brought within the means of the Indian masses whose economic condition is unfortunately of a very low order

A number of important drugs, extensively used by the medical profession, however, are neither found wild nor have so far been cultivated in India. Cultivation of such drugs is very important from an economic point of view, and scientific research in this direction, as is being carried out in other countries, would be very fruitful. It is a matter of regret that India is still importing large quantities of crude drugs in spite of the fact that practically every conceivable pharmacopoeial drug can be grown within her bounds. The history of the cultivation of cinchona, eucalyptus, digitalis, etc. in India clearly shows that the cultivation of medicinal plants is pregnant with rich possibilities if taken up on proper lines. It is gratifying to note that more and more interest is now being taken in this direction. A list of medicinal plants which might with advantage be cultivated has been prepared and is available for those interested in such development.

Remedies used in Indigenous Medicine

Our second objective has been to discover remedies from the claims of Ayurvedic, Tibbi and other indigenous resources suitable for employment by exponents of Western medicine. Since the period of decay and resuscitation of old systems of Indian medicine, many of the effective remedies have been lost while a number of uncertain ones have crept in. Belief in their efficacy originates in some cases from the teachings of the ancient commentators and is based on clinical data, but in others has no foundation whatever. Nearly two hundred medicinal plants have been investigated in our laboratories and some of these have been shown to be of practical utility. Apart from this, the negative value of such investigations should not be lost sight of. Whatever the merits or demerits of the indigenous systems may be, it should be remembered that they minister to the needs of nearly 80 per cent of the population of this vast country. It is, therefore, the primary duty of any research organization existing in this country to evaluate their effectiveness and practical utility.

Collection of drugs

A few words may be said here with regard to the time of collection of drugs. During the last twenty-five years several drugs of Indian origin have assumed considerable importance from the point of view of foreign trade. Many firms of drug manufacturers in this country also use the locally produced raw materials for the manufacture of the finished products. It is a matter of very great concern, therefore, that the crude drugs collected locally are often not up to the required standard and this has resulted in considerable economic loss. Fortunately, this state of affairs is being gradually rectified but I cannot let this opportunity pass without reiterating that collection of drugs is not so simple a matter as most people seem to imagine. Collectors of medicinal drugs growing in a state of nature, and the present and prospective cultivators should bear in mind that there are certain factors which have to be considered in order to obtain the standard product. There is a good deal of variation in the active principles in the different parts of a plant and in different seasons in the same part of the plant. Even the same part and at the same time of the year shows remarkable variations in the contents of its active principles, for example, the young and the old leaves of a plant and unopened and opened flowers differ materially despite the fact that they are collected from the same plant and during the same season The soil also has an important influence on the active principles of plants I have often observed in the course of my work that plants collected at the proper time, when the active principles have reached maturity and are at their maximum, give very effective results while the same plants when collected under other conditions are utterly useless Conditions for the collection of drugs in the case of plants under cultivation are more favourable and strict control over various factors can be exercised with greater ease than is the case with plants growing in a state of nature It has, however, to be admitted that ideal conditions for the collection of even many of the common and important medicinal plants are not known with precision, and research is urgently needed to determine the time when the active principles are at their maximum under the environments existing in this country, as was done by the Dutch in Java in the case of cinchona If this could be systematically carried out, India could supply the whole of the world with medicinal 'herbs'

Poisonous Plants

General consideration and loss to India

Intimately connected with the study of medicinal plants is the problem of poisonous plants, but till recently little attention has been paid to this study in this country They contain chemical constituents which, if introduced into the body of an animal in relatively small quantities, act deleteriously and may cause serious impairment of bodily functions or even death They injure the basic live principle, the protoplasm, of the cells of which the animal body is built up They are ordinarily called poisonous plants, and apart from the utilization of their potent properties in the treatment of diseases to alleviate the sufferings of man and animals, there appears to be no doubt that they are a source of great menace in India through poisoning of livestock.

Poisoning of livestock

We are concerned in this country with the welfare of 360 millions of human beings, as well as with that of roughly 220 millions of the bovine population out of a total of about 730 millions in the whole world Even in its present unsatisfactory condition, the cattle industry contributes roughly about 10,000 million rupees to the annual agricultural income of 20,000 million rupees of this vast country. The importance of plants which are poisonous to livestock will thus be readily understood It is a matter of regret that no systematic attempt has been made in India so far to investigate these plants on scientific lines with a view to devising means whereby this menace could be controlled It is also unfortunate that no figures are available of the loss suffered by India through poisoning of livestock by this agency, but it may be interesting here to give the example of two States, Montana and Colorado in the United States of

America, which may give us some idea of the possible damage In that area it has been estimated that the loss inflicted to the livestock industry by plant poisoning is in the neighbourhood of 220 million dollars annually This is a very high figure considering that the size and extent of these States as compared with India is less than one-sixth, and also considering the fact that the knowledge regarding the poisonous plants there is well advanced and preventive measures are practised The conditions existing in India can be readily imagined.

Study of Poisonous Plants

With a view to combating this menace, and as a natural corollary to the study of medicinal plants, the study of poisonous plants of India has been undertaken at the School of Tropical Medicine during recent years This work has brought out some outstanding features of the problem which had not been hitherto appreciated in India About 700 poisonous species belonging to over 90 families of flowering plants are known The more important of these in their order of importance are Ranunculaceae, Euphorbiaceae, Leguminosae, Solanaceae, Compositae, Apocynaceae, Asclepiadaceae, Ericaceae, Liliaceae, Gramineae, Araceae, Anacardiaceae, Thymelaeaceae, Rosaceae and Rubiaceae As in the case of medicinal plants, it does not mean that other families do not contain important poisonous plants In fact there are several other families which have a few of the very potent species belonging to this group The above list of the important families merely indicates that they contain the largest number of poisonous plants, so far as is known at present, with a further likelihood of containing plants with potent principles which are at present unknown

In the case of the majority of plants, poisonous properties are only suspected but have not been substantiated by chemical analyses and pharmacological experimentation This is now being done, so far as possible, preliminary chemical examinations of a large number of plants have been made and a monograph on the subject is now in press A thorough and comprehensive study of all these plants, however, would mean sustained work for many years and perhaps for several generations In the present work we are getting together all the information, botanical, chemical and pharmacological, with detailed references to the literature This monograph, when completed, should serve as a basis for further work on these plants, the importance of which from an economic point of view cannot be overrated Increased knowledge with regard to their distribution and the nature of active principles responsible for poisoning is the first step towards controlling this problem by taking preventive measures

Insecticidal and insect repellent plants

Another aspect of these plants which will repay study concerns those which have insecticidal and insect repellent properties. Losses inflicted upon India by insects are enormous and at a moderate estimate are calculated at 2,000 million rupees annually and over a million and a half of human lives Effective defence against these enemies of social and economic progress should materially reduce this enormous wastage and facilitate national development The finding of cheap insecticides for the diverse needs of agriculture, destruction of household pests, prevention of vectors of such diseases as malaria and many others borne by insects, commensurate with the limited means of the great masses in India, are important problems to which little attention has been paid till recently Vegetable insecticides are preferable to mineral ones, as these are less deleterious to man and other warm-blooded animals generally, and as they are also less harmful from the point of view of agriculture Lists of the possible insecticidal and insect repellent plants growing in India, and of reputed fish poisons some of which may also act as insecticides have been prepared

Herbarium of Medicinal and Poisonous Plants

One of the chief difficulties in connection with our work on medicinal and poisonous plants has been the proper identification of the material to be investigated The descriptions of plants given in the literature on indigenous medicine are meagre and vague and this has resulted in considerable confusion Many drugs are sold under different names, different drugs under the same name, and even the learned *Kavirajs* and *Hakims* cannot say with certainty which species are meant in the old text-books No authentic specimens of even the well-known remedies were ever collected and preserved by the exponents of indigenous medicine and no actual comparison is possible Even with the great advances in systematic botany, expert botanical identification is not infallible and the botanists also sometimes prefer to disagree Publications of recent botanical monographs show, how with the advance of knowledge our conception of species has varied Descriptions alone are not always sufficient for settling disputed questions and recourse to actual specimens is often absolutely necessary It is very important, therefore, to preserve specimens of all plants submitted for investigation, so that these may be available for reference in case any doubt as to their identity arises at a later date Some of the chemical and pharmacological work done on these plants has been vitiated by carelessness in identification With a view to combating this state of affairs it was considered desirable to collect authentic specimens of all the plants with alleged medicinal or toxic properties and after proper identification preserve them for the purpose of comparison This work has progressed and it has been possible to collect 6,000 specimen sheets of about 1,600 species About 900 species have yet to be obtained to complete the collection of all the known medicinal and poisonous plants growing in India As most of the more easily available plants have been obtained, the collection of the remainder is becoming more and more difficult but the work is being continued When this is accomplished, this collection will be the first of its kind in India, and should be an asset both from the scientific and economic points of view The present collection will, it is hoped, form the nucleus for a national herbarium of medicinal and poisonous plants

Survey of Medicinal and Poisonous Plants in India

A question of great economic importance is the working out of the distribution of medicinal and poisonous plants in this country The distribution of many plants as described in literature is often vague and inaccuracies, which have crept in, have been passed down from one publication to another To this may be added the fact that plants which were found in a particular locality some years ago often do not occur there at the present day The influence of man in changing forests into agricultural lands and sometimes again abandoning them to the care of nature, together with the competition of plants amongst themselves is materially responsible for the change in the floras of various areas For this reason we started the stock-taking of the present distribution of medicinal and poisonous plants to work out, as exactly as possible, the present areas of their distribution All the available literature is being consulted and herbaria all over India are being scrutinized Personal visits are being paid to different parts of India to determine the areas of abundance of these plants growing in a state of nature The work under this head is very extensive when it is remembered that it deals with about one-fifth of the total number of plants found in India, but this is the only way of estimating with any degree of accuracy whether a certain plant grows well and in abundance or is scarce in a certain area Valuable information is thus being collected, and this will be of practical value to those interested in harnessing the natural resources of the country This will also give indications of suitable localities for the cultivation of medicinal plants

From the point of view of poisonous plants also, this survey is of great practical value, as once the occurrence of the harmful herbage in grasslands and other localities open to grazing for livestock are mapped, it should be possible to adopt measures for the protection of livestock against the menace of poisoning

Correlation of botanical classification of plants, their chemical constitution and their physiological properties

Active principle and new classification

With the advance of knowledge of the chemistry and pharmacology of plants, it appears to be certain that some correlation exists between the botanical classification of plants, their chemical constitution and physiological properties, and one is frequently struck with the remarkable resemblance exhibited by closely allied plants in this respect For example, if a particular chemical constituent is found in one member of the genus, there is considerable likelihood of the presence of constituents with identical or similar physiological properties in other members of the genus or of the family This does not, of course, mean that such similarity will not be found in other families or genera just as particular taxonomic characters may be spread over widely different families and genera An ideal classification of plants would be the one which in addition to satisfying botanical criteria broadly provides an index to the nature of their chemical constituents and physiological properties With our existing knowledge this is not possible The very fact that some of the families and genera, as at present understood, are quite homogeneous in these respects, however, reflects a ray of hope that after all the problem is not so difficult as it appears at first sight Considerable work on the chemistry of plants and the determination of the physiological properties of their active principles, however, will have to be carried out and thousands of new plants will have to be investigated before this is attained, or the attempt given up as hopeless This should not, however, be understood to imply that I suggest that advances in the knowledge of chemistry and pharmacology should determine the botanical classification of plants This is not possible, as such features cannot possibly serve as taxonomic characters But I do hope that botanists, chemists and pharmacologists will collaborate in evolving a natural system of classification based on their combined efforts

Chemical Constituents

A brief review of the distribution of the more important and potent chemical constituents of the Indian flowering plants of widely different families and genera presents certain very interesting features The alkaloids are distributed over about 40 families and there are a number of cases where the same alkaloid is found in closely allied genera and families Thus, berberine has been recorded from six different families and twelve genera Ephedrine, on the other hand, furnishes an example wherein a particular alkaloid may be found in plants belonging to widely different groups, it has been found in *Sida cordifolia* Linn of Malvaceae (a family belonging to Angiospermae) and in *Ephedra* of Gnetaceae (a family belonging to Gymnospermae) Purines are found in three families The glucosides form a large group and are much wider in occurrence than the alkaloids, occurring both in Dicotyledons and Monocotyledons; some of these are very toxic and occur in eight widely different families Hydrocyanic acid yielding plants belong to ten families A group of glucosides known as saponins is of very wide occurrence in the vegetable kingdom, saponins are known from at least 400 plants belonging to 50 different families occurring almost all over the world Essential oils are of wide occurrence in the vegetable kingdom though certain families, such as Labiatae, Rutaceae, Umbelliferae, Myrtaceae, Lauraceae, Cruciferae and Coniferae are especially rich in these substances. The seeds of numerous plants contain albumins, but it is interesting to note certain plants, such as *Abrus precatorius* Linn and *Ricinus communis* Linn belonging to very different families (Leguminosae and Euphorbiaceae respectively) wherein the toxicity of these albumins is of a similar nature, both being essentially blood-poisons, and both similar in their immunity reactions if introduced into the body of animals in small and gradually increasing doses.

I do not propose to go into further details of several other chemical constituents, nor even of such toxic complexes as resins, phenolic compounds, etc. The few examples cited provide sufficient evidence in support of the now well-established theory of organic evolution. I repeat that there is a method in their occurrence, in several cases it is due to their descent from common ancestors while in others it is a result of parallel evolution. The facts described above cannot be explained on any other basis.

Examples of correlation

I will now cite a few examples of some families and genera to show the marked resemblances between their botanical, chemical and pharmacological aspects. Unless definitely proved as harmless it is advisable, for instance, to regard all members of Ranunculaceae as potentially poisonous, especially when fresh, both for human beings and livestock. Poisonous, acrid, vesicant purgative and narcotic properties prevail in varying degree throughout the family. Species of *Anemone*, *Caltha*, *Clematis* and *Ranunculus* contain the lactone anemonin which has blistering properties. Most of the Aconites contain highly poisonous alkaloids which act mainly on the sensory nerves and on the medulla which they depress and ultimately paralyse. Species of *Delphinium* are used for the destruction of vermin and contain toxic alkaloids, some of which appear to act like aconitine, while others paralyse the motor nerves. Alkaloids are also known to occur in the genera *Coptis*, *Helleborus*, *Nigella*, *Isopyrum* and *Paeonia*. *Adonis* and *Helleborus* contain glucosides with a digitalis-like action. Saponins are found in the genera *Clematis*, *Ranunculus*, *Nigella* and *Cimicifuga*. Cyanogenetic compounds have been reported from some of the members of the family and the Indian representatives from which these principles have been reported belong to the genera *Clematis*, *Aquilegia*, *Isopyrum* and *Ranunculus*. Seeds of *Annona* of Annonaceae have insecticidal properties and are powerful irritants of the conjunctiva. Several species of *Berberis* contain active principles poisonous to fishes and dogs. Many species of *Papaver* have a juice with narcotic properties and contain powerful alkaloids. Narcotic properties are also possessed by some other members of the family Papaveraceae, e.g., *Meconopsis*. Most Crucifers have pungent juices and many have glucosides in their seeds and produce very irritant essential oils, they possess stimulant properties. Several plants of Caryophyllaceae contain saponins. The family Rutaceae is characterized by the presence of essential oils some of which are toxic. Many plants belonging to Sapindaceae have saponins and a number of them are well known as fish poisons. Anacardiaceae are usually provided with more or less acrid resinous, sometimes milky juices, very many species of this family possess astringent properties. Plants of no less than twenty-seven genera of Leguminosae possess insecticidal or piscicidal properties. The poisonous properties of Rosaceae are generally due to the presence of cyanogenetic compounds. The presence of powerful bitter and purgative principles is the prevailing characteristic of the wild members of Cucurbitaceae. Aromatic members of Umbelliferae are usually carminative, while the non-aromatic members are often acrid and narcotic and should be taken with care. Alkaloids with similar physiological properties are the outstanding constituents of the genus *Cinchona* Lobelias belonging to Campanulaceae yield an intensely acrid milky juice and the dust of the powdered herbs irritates the nostrils in the same way as tobacco, they contain alkaloids Rhododendrons mask, under the beauty of their flowers, very fatal active principles and the family Ericaceae to which they belong contains several insecticidal plants, the toxic substance andromedotoxin is very common in this family Apocynaceae includes several plants which are highly poisonous, the properties of most of them being due to glucosides with a digitalis-like action and physiologically active alkaloids Many species of Asclepiadaceae contain acrid, bitter and poisonous juices The genus *Strychnos* is rich in alkaloids which are violent tetanic poisons Many species of Convolvulaceae have an acrid taste and contain active purgative principles Mydriatic alkaloids such as atropine, hyoscine and hyoscyamine are found in several species of Solanaceae while the glucosidal alkaloid solanin is found in many Solanums and some other genera as well, a very large number of wild plants of this family are poisonous Labiatae is very uniform in the possession of essential oils, several of which are of medicinal value as carminatives and stimulants Toxic resins are reported from a number of species belonging to Thymelaeaceae and animals avoid eating them Several species of Euphorbiaceae contain more or less acrid and irritant juices and several species of Crotons contain highly irritant toxalbumins and are drastic purgatives Urticating principles are found in four Indian genera of Urticaceae The alkaloids ephedrine and pseudo-ephedrine are found in a number of Ephedras Coniferae are characterized by containing essential oils which produce gastro-intestinal irritation and sometimes ulceration Several species of Dioscoreaceae contain an acrid juice in their tubers and some are even poisonous Quite a number of species of Araceae contain raphides of calcium oxalate and acrid juices, a number of these plants, if eaten, especially when in fresh condition, produce symptoms of irritant poisoning Some of the Gramineae, especially when young, wilted or under drought conditions produce hydrocyanic acid and are fatal to livestock, no alkaloid has so far been isolated from members of this family

Many more examples could be cited, but the brief review of the relationship which seems to exist between the botanical classification and the chemical and physiological characteristics of medicinal and poisonous plants should prove sufficient to show that in many of the families and genera these characteristics show a marked degree of correlation I do hope that further work will produce increasing evidence of this relationship The botanical characters, chemical constituents and properties exhibited by plants are all the results of organic evolution and a natural classification must embrace all these three aspects There is, however, an element of disturbance in the case of plants Climate, seasons, soil, cultivation, etc , have profoundly affected their chemical composition and hence their physiological characteristics, and it is for this reason also that closely related plants differ in their pharmacological properties

Conclusion

The above brief review of our work on the medicinal and poisonous plants, the difficulties encountered and partially overcome, and indications in regard to their utilitarian and scientific aspects, will, I hope, stimulate interest in this subject which is of considerable economic importance to the country, particularly at the present juncture. Collaboration between botanists, chemists, pharmacologists and agriculturists in work of the type indicated in a country such as India, with all extremes of meteorological, climatic and topographical features resulting in very varied and luxuriant floras of all types is pregnant with possibilities which should not only be of very great scientific and academic interest but also prove of great practical importance to the country from the economic point of view.

ON THE STRUCTURE OF ATOMIC NUCLEI

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(*Received January 16, 1940*)

Ever since Heisenberg (1932) showed that the nucleus of the atom is to be regarded as composed of two fundamental particles, viz, the proton and the neutron, many investigations from the theoretical point of view have been carried out regarding the structure, stability and reactivity of nuclei In the meantime, there have been large additions to the known number of nuclei by (1) the discovery of newer and rarer stable isotopes, and (2) the discovery of new unstable varieties of isotopes produced by bombardment of known nuclei by means of α-particles, deuterons, protons, neutrons and to a slight extent by photons The recent discovery of fission of uranium and thorium by neutrons has led to the discovery of a number of β^--active nuclei which probably could not have been produced by any other existing method

The enormous increase in our knowledge of nuclear phenomena within the last eight years has rendered it almost impossible for the average physicist to form a comprehensive picture of the present situation, much less than keep in living touch with progressing knowledge

In this paper, an attempt has been made to present the existing knowledge of the known nuclei, stable, as well as radioactive, in the form of a chart No attempt has been made to give any theoretical discussion on stability in this paper, but rules and regularities which are obvious have been duly noted and recorded Probably we are justified, at this stage, in adopting this attitude in view of the following significant remark we came across in Gamow's 'Structure of Atomic Nuclei' (1938)

'One may hope that further investigations along these lines will add considerably to our understanding of more detailed problems of structure Much has already been done with rather overlapping results by Bartlett, Gapon, Ivanenko, Elsasser, Guggenheimer and others, it is not referred to in detail here because the author was never able in studying these articles to remember the beginning when he was reading the end '

Symbols used

We denote by

p the proton,
n the neutron,

Z	the nuclear charge,
N	the number of neutrons,
A	the mass-number, so that $A = Z+N$

$I = N-Z = A-2Z$ has been called the '*Isotope-number*' by Bethe and Bacher (1936)

According to this notation

$p^Z n^{Z+I}$ or $p^Z n^N$ denotes a nucleus composed of Z protons and N neutrons Thus ${}_{38}Sr^{87}$ is $p^{38} n^{38+11}$, *i e* strontium 87 would be found in the isotope line $I = 11$ of our chart

In this connection, a comparison may be made between the chart given here and the other charts so far in use Papers earlier than 1931 were written on the supposition that the nucleus was composed of protons and electrons Nevertheless, many of the conclusions and regularities noted in earlier papers are very valuable, and have been utilized by subsequent workers

(1) W D Harkins (1928) plotted an (I/Z)-curve in fig 14, p 113, and nuclei were classified into a few groups

(2) Barton (1930) plots an (N/Z)-diagram up to $Z = 61$, and notes a few regularities

(3) W D Harkins (1931) plots an (N/Z)-diagram (fig 1) and a number of (I/Z)-diagrams (figs 2, 3, 4, 5) and an (N/P)/Z-diagram

(4) Heisenberg (1932) first took the view that the nucleus is composed of neutrons and protons He discussed nuclear stability by plotting (N/Z)/Z-diagrams

(5) Gamow (1934) utilized (N/Z)/Z-diagrams for a discussion on nuclear stability and α- and β-emissions

(6) Guggenheimer (1934) plotted an (N/Z)-diagram and classified nuclei into groups

(7) Bethe and Bacher (1936) give on p 97 an I/A-diagram on a small scale, comprising only stable nuclei No isotopic lines (Z-lines) have been drawn, but some regularities regarding the stability of nuclei have been pointed out

None of the above workers included β^{+-}-emitting nuclei in their diagrams

(8) Hevesy and Levi (1936-37) have given a number of (I/Z)-diagrams of stable and radioactive isotopes

(9) H Brown (1938) has plotted an (I/Z)-diagram for finding out the range of occurrence of stable isotopes

(10) Gregoire (1938*a*) has an (A/Z)-diagram for presenting the totality of our knowledge of nuclei, stable as well as radioactive (The same diagram has been drawn more elaborately in '*Physique Nucleaire*' *of Tabelles Annuelles de Constant et Donneé's Numeriques No* 26, 1938) Here the radioactive nuclei have been drawn in different colours, and percentages of isotopes have been indicated

(11) In their paper on 'Mechanism of Nuclear Fission', Bohr and Wheeler (1939) published an (I/A)-diagram (Fig 8, p 445) for illustrating 'Nuclear Fission' This paper came to our notice after our work was almost over This figure contains only stable nuclei and is identical in principle with ours, but it has been drawn for a limited range, and for illustrating the successive β^--emission products of fission of the uranium nucleus

Explanation of the chart

The abscissa represents mass-number A, the ordinate represents I, the isotope number The parallel lines at 45°, to be henceforward called the Z-lines, represent atomic number 'Z' Thus all isotopes of element 'Z' are to be found on the same 'Z'-line Each isotope is represented by a circle Solid circles represent 'Stable' nuclei Hollow circles with an arrow pointing up, $\overset{\uparrow}{\bigcirc}$, represent β^+-emitting (positron) nuclei, when the arrow points down, $\underset{\downarrow}{\bigcirc}$, they indicate β^--emitting (electron) nuclei Circles with arrows pointing both up and down, $\overset{\uparrow}{\underset{\downarrow}{\bigcirc}}$, like $_{29}Cu^{64}$ indicate that the nuclei are both β^+ and β^--active The percentage occurrence of any nucleus is given by the number on the top For isotopes having small abundance, the actual percentage is given to the nearest fraction The half lives of β-particle-emitting products are indicated The following abbreviations have been used for indicating the half lives

s	seconds,
m	minutes,
h	hours,
d	days,
mo	months,
y	years

The nuclei represented by $\underset{\downarrow}{\ominus}$ denote those obtained by fission of U or Th

The reader may now refer to the symbolic diagram on the left of Chart 1 The N W -pointing arrow terminating in *p* denotes a proton-emission, an arrow in the opposite direction (S E , not shown in fig) denotes a proton-capture

Similarly, the S W -pointing arrow ending in *n* denotes neutron-emission, and an arrow in the opposite direction (N E , not shown in fig) would denote a neutron-capture

The west-pointing double-arrow terminating in α denotes an α-particle-emission

Thus we can follow the reaction

$$B^{10}+H^1 = C^{11}+h\nu, \quad C^{11}\rightarrow\beta^+ = B^{11}$$

in the chart by putting our finger on B^{10}, and going diagonally downwards (S E) we reach C^{11}, and we find that C^{11} will emit a positron, and going vertically upwards we reach the stable nucleus B^{11}

'Neutron-capture' takes a nucleus a step higher along the Z-line

Thus

$$Be^9+n^1 = Be^{10}+h\nu \ (?)$$

$$Be^{10}\rightarrow\beta^- = B^{10}$$

We can follow this reaction easily in the chart Let us take a reaction in which a nuclear particle is emitted, *e g*,

$$Ca^{42}+n^1\rightarrow Ca^{43*}\rightarrow K^{42}+H^1$$

$$K^{42}\rightarrow\beta^- = Ca^{42}$$

We put our finger on Ca^{42}—a neutron bombardment of Ca^{42} followed by capture takes us to Ca^{43*} along the Z-line, * denoting that it is an intermediate nucleus, of extremely short life, breaking up into K^{42} and H^1 K^{42} is obtained by going diagonally up in the p-direction The chart shows that K^{42} is β^--active and changes to Ca^{42}

Deuteron-bombardment

Deuteron bombardment followed by capture will take a nucleus along the I-line (horizontal or East) to the next nucleus, and the chart tells us what reactions are to be expected Thus

$$Si^{30}+H^2\rightarrow P^{32*} = Si^{31}+H^1$$

We put our finger on Si^{30}, capture of H^2 takes us to P^{32*} intermediate, which breaks up into Si^{31} and H^1 The chart shows that Si^{31} emits a β^--particle and gives us P^{31} Thus starting from Si^{31} one goes vertically one step downwards and reaches P^{31} The reaction $P^{32}\rightarrow\beta^- = S^{32}$ is also possible, but its probability seems to be negligibly small

α-ray bombardment.

α-ray bombardment followed by capture will take a nucleus along the I-line two steps to the right, and *vice-versa*, if in a reaction, an α-ray is emitted, the nucleus will have to be taken two steps to the left along the same I-line

Thus

$$N^{14}+He^4\rightarrow F^{18*} = O^{17}+H^1, \text{ or } F^{18*}\rightarrow\beta^+ = O^{18}$$

Thus we see that N^{14} on capturing He^4 will form an intermediate nucleus F^{18*}, which can either break up into O^{17} and H^1, or emit a β^+-particle, and pass on to O^{18} The former process is, however, much more probable and is observed usually.

For illustrating the use of the chart, we take sulphur, Z = 16 A glance at the Z-line 16 shows that sulphur has the following isotopes

S^{31}	S^{32}	S^{33}	S^{34}	S^{35}	S^{36}	S^{37}
+	95	7	4	—	02	—
26*m*(?)				88*d*		5*m*

S^{31} is β^+-active, with half life of 26*m* ? indicates that the estimate is doubtful S^{35}, S^{37} are β^--active, with half lives 88 days and 5 min respectively S^{32}, S^{33}, S^{34}, S^{36} are stable isotopes occurring in the proportion 95 7 4 02

The symbol $\overset{\uparrow}{\circ}$ indicates that the nucleus $p^Z n^{Z+1}$ does not actually emit a positron, but captures a K-electron, and passes on vertically up to the nucleus $p^{Z-1}\ n^{Z-1+1+2}$

A glance at the chart at once shows its usefulness It not only comprises all our present knowledge about isotopes, stable as well as radioactive, but, as will be shown presently, indicates definite rules for stability and for electron- and positron-emission Further, it suggests new nuclear processes and predicts new stable isotopes, not yet discovered For purposes of clarity, a number of I-lines at intervals of '5' have been drawn These have no special significance

Rules for Stability

For discussing this point, we have taken each horizontal row, corresponding to definite values of 'I'

If we take I = 0, we find that the nuclei are stable from Z = 1, H^2, to Z = 8, O^{16} After that, the nucleus is stable for even values of Z, and β^+-active for odd values of Z The group stops with Sc^{42}, which is β^+-active

(Rule 1).

When I is even and > 2, we get alternation of stable and β-active nuclei Stable nuclei are obtained for *even* values of Z and β-active nuclei are obtained for *odd* values of Z This rule is partly foreshadowed in a remark by Bethe and Bacher (1936, p 104) and has been discussed in detail in §10, p. 100

Illustration

Let us take I = 4 We get the following —

I = 4, Z =	16	17	18	19	20	21	22	23
	S^{36}	Cl^{38}	A^{40}	K^{42}	Ca^{44}	Sc^{46}	Ti^{48}	V^{50}
	stable	—	stable	—	stable	—	stable	+
Z =	24	25	26	27	28	29	30	31
	Cr^{52}	Mn^{54}	Fe^{56}	Co^{58}	Ni^{60}	Cu^{62}	Ni^{64}	Ga^{66}
	stable	+ —	stable	+ ?	stable	+	stable	+

We observe that after approximately the middle of the series is passed, the nuclei to the right with odd Z become β^+-active This rule is found to be obeyed right up to I = 40, after which we enter the region of natural radioactivity, where also up to I = 54, the rule is generally obeyed with a few exceptions (noted later)

For I = 2, we observe that the first stable nucleus is Z = 8, O^{18}, after which the rule of alternation holds all right Before Z = 8, we have a number of β^--emitting nuclei from Z = 1 to Z = 7 It is quite possible that in the other groups also, *e g* for the group I = 4, we may have a number of β^--active elements before S^{36}, but special reactions will have to be devised to obtain them

(Rule 2). I is odd

In these groups, we first find β^--active nuclei, and then arrive at *a number of succeeding stable nuclei* These are followed by β^+-active nuclei The number of succeeding stable nuclei has been found sometimes as small as 3, sometimes as large as 13, usually the nucleus in the midst of the stable group appears to be the most stable, though there appear to be exceptions

Illustration

Let us take I = 5 A glance at the chart shows that we have

I = 5, Z =	16	17	18	19	20	21	22	23
	S^{37}		A^{41}	K^{43}	Ca^{45}		Ti^{49}	V^{51}
	—		—	—	—		6,	100,
Z =	24	25	26	27	28	29	30	31
	Cr^{53}	Mn^{55}	Fe^{57}	Co^{59}	Ni^{61}	Cu^{63}	Zn^{65}	Ga^{67}
	10,	100,	2,	99 8	1,	68,	+	+
Z =	32	33						
	Ge^{69}	As^{71}						
	+	+						

The stable nuclei start from Ti^{49} and extend up to Cu^{63} The numbers below them here show the percentages The elements to the left of the stable group are β^--active and those to the right are β^+-active We have some gaps, *e g*, at Cl^{39} (β^-), Sc^{47} (β^- or stable), but these will probably be discovered if proper nuclear reactions are tried

We now begin a detailed discussion of the table, taking each I-line in turn While studying these discussions, the reader is advised to have the chart at hand, as all references are to the chart

I = −2·

A few nuclei like Li^4 have been postulated, but as knowledge about them is very meagre, we leave this group for the present out of our consideration.

$I = -1$

In this line, H^1, He^3 (Alvarez and Cornog, 1939) are stable Li^5 cannot be formed, energy-considerations are against it

Absentees are —Na^{21}, P^{29}, Cl^{33}, A^{35}, K^{37} which are expected to be β^+-active

The series terminates at Sc^{41}

It is probable that the 'absentee' nuclei may be obtained if proper nuclear reactions are tried Let us take an example

For Na^{21}, the following reactions are suggested –

$$(1)\ Ne^{20}+H^1 = Na^{21}+h\nu$$

This is suggested in analogy to the reaction $O^{16}+H^1 = F^{17}+h\nu$ which has been observed by DuBridge *et al* (1937, 1938)

$$(2)\ Ne^{20}+H^2 = Na^{21}+n^1$$

This is suggested in analogy to the reaction $O^{16}+H^2 = F^{17}+n^1$, observed by Kurie *et al* (1936) and Newson (1937) But the reaction has been tried by Snell (1937) who, however, obtained $Ne^{20}+H^2 = F^{18}+He^4$ Probably the chance of capture followed by γ-emission is negligible to that of particle emission, as has been found by Bethe (1939)

It is clear from this discussion that the suggestion of proper reaction to get a certain absentee nuclei will involve a good deal of work Hence the subject is not further pursued in this paper

It is not yet clear whether there will be any limit to the number of nuclei on any I-level The last nuclei for $I = -1$ is Sc^{41} It is possible that we may get the series continued to Ti^{43}, V^{45}, etc , but the prospect of getting such nuclei will be diminished with larger Z, as *no* stable nuclei, which can act as the starting material for bombardment with H^1, He^4 and n^1 will be available

$I = 0$

This line starts with H^2 and is stable up to O^{16}, after which the alternation rule holds Nuclei are stable for Z = even, and β-active for Z = odd The series terminates for Sc^{42}, but we have, after a long interval, Cu^{58}, which is stated by Delsasso (1939) to be β^+-active The intermediate absent nuclei are —

Ti^{44}	V^{46}	Cr^{48}	Mn^{50}	Fe^{52}	Co^{54}	Ni^{56}
St	+	St	+	St	+	St

which may be looked for

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$I = 1$

H^3 is β^--active, as has been shown by Alvarez and Cornog (1939*b*) changing probably to stable He^3, and after that we have stable elements up to Cl^{35} in an unbroken series K^{39} has been shown to be definitely stable Hence A^{37} ought to be stable, and may be a very rare isotope Ca^{41} is still unknown, and as it is on the border line, we cannot say whether it will be stable or

β^+-active. From Sc^{48} to Ni^{57}, all are β^+-active with the exception of Ti^{45} and V^{47} which have to be looked for

$I = 2$

We have β^--active nuclei from H^4, (rather doubtful) to N^{16}, and then we have alternation of stable and radioactive nuclei beginning from O^{18} From Sc^{44}, the radioactive nuclei in this group begin to become β^+-active and with the exception of Zn^{62}, which may be looked for, we have the group extended up to Ga^{44}

$I = 3$ ·

In this group, the stable nuclei start from Cl^{37} and end in Ti^{47} On the left side, they are flanked by β^--active nuclei which, with gaps at F^{21}, Na^{25} and P^{33}, can be traced to O^{19} The group contains the notable anomalous nucleus A^{39} which ought to be stable, but Nier (1936) who specially looked for it states that its abundance is less than 10^{-5} of the most abundant isotope A^{40} Gregoire (1938*b*) gives it as β^--active, but doubtfully The anomaly ought to be cleared up

On the right side of the last stable isotope Ti^{47}, the nuclei are all β^+-active, with the exception of Co^{57} which according to Bleakney *et al* (1936) is stated to be stable with an abundance of 18 per cent If it is really stable, it forms a glaring anomaly which ought to be cleared up

The line is continued to Zn^{63} at present, but further β-emitting particles may be discovered on both flanks

$I = 4$ ·

In this line, as in all with even values of I, the rule of alternation regarding stability is followed, without exception The limits of the line at present are left S^{36} (stable) and right Ga^{66} (β^+-active) Co^{58} should be β^+-active, but the nature of the particles emitted has not yet been ascertained experimentally

In this and all other groups with *even* values of I, it is still a moot question whether, if the line is extended on both flanks, the nuclei will continue to obey the law of alternation, *e g*, whether Si^{32} or Mg^{28}, if discovered, will be stable or β^--active Similarly on the right flank whether Ge^{68} or Se^{72}, if discovered, will be stable or β^+-active A third possibility is that like Li^5, they may be energetically impossible These remarks apply to the subsequent discussions

One difficulty in the formation of these 'flank' nuclei would be that of getting any 'starting'-point This point may be illustrated by a concrete example Let us take C^{16} and N^{18} which fall in the line $I = 4$ Now C^{16} should be stable if rule (1) is obeyed, and N^{18} ought to be β^--active But from what nucleus should we start to get C^{16}? Since O^{18} is stable, it may be possible to produce N^{18}, but B^{14} will again be difficult to produce

According to present ideas of stability, all such nuclei may be β^--active, but actual experiments can alone decide how far the rule of alternation will extend on both flanks.

As will be seen later, some 'flank' nuclei of the description given here have been obtained in the case of $_{52}$Te to $_{58}$Ce and $_{35}$Br to $_{40}$Zr by the fission of the uranium nucleus But the fission process is probably possible only for the heaviest nuclei

I = 5

We have in this line 8 stable nuclei from Ti^{49} to Cu^{63}, flanked by β^--emitting nuclei on the left, and β^+-emitting nuclei on the right Sc^{47} may be a stable nucleus or β^--active Cl^{39} will be β^--active

From I = 6, the rules we have stated appear to be followed rigorously The remarks with respect to 'flank' nuclei are always to be taken subject to the observations made under I = 4

I = 6

Absentees are As^{72}, Br^{76}, both β^+-active

I = 7

This line shows only three successive stable isotopes at Cu^{65}, Zn^{67}, Ga^{69} There are gaps at V^{53}, Cr^{55}, Mn^{57}, Co^{61} (all β^--active) and at Br^{77}, Kr^{79}, Rb^{81}, Sr^{83}, Zr^{87} and Nb^{89} (all β^+-active) which may be looked for

I = 8

This line is very much broken We have the first stable isotope Ca^{48}, and then after a long pause Ni^{64} Search may be made for

Sc^{50}	Ti^{52}	V^{54}	Cr^{56}	Mn^{58}	Fe^{60}	Co^{62}	Y^{86}	Zr^{88}	Nb^{90}
−	stable	−	stable	−	stable	−	+	stable	+

Some of these stable isotopes have been looked for by Nier (1938), but have not been obtained He states that Ti^{52} is $< 10^{-5}$, Cr^{56} $< 10^{-5}$, Fe^{60} $<$ 3×10^{-5}, Zr^{88} $< 10^{-5}$, of the respective most abundant isotopes, if they exist at all

I = 9

We have here stable isotopes from Ga^{71} to Br^{79} β^+ active isotopes are expected at Rb^{83}, and Nb^{91}

I = 10

This series starts with the stable isotope Zn^{70} and is continued up to Cd^{106} Ru^{98} ought to be stable and we may look for β^+-active nuclei at Rh^{100} and Ag^{104}

I = 11

This group contains *11* successive stable isotopes from Br^{81} to Rh^{101} To this group also belongs Ma^{97}, still undiscovered The first β^+-active nucleus is Cd^{107} shown as doubtful There are two intervening absent nuclei, Pd^{103} and Ag^{105}, which may be β^+-active. Ga^{73} may be β^--active.

I = 12

This group starts with the stable nucleus Ge^{76} and is continued up to Sn^{112}. There is one absentee at In^{110} which may be β^+-active

I = 13

The stable group starts at Mo^{97} and is continued up to Ag^{107} Ma^{99} is expected to be stable and one of the chief isotopes of the element, which is still undiscovered As^{79}, Y^{91} and Nb^{95} may be β^--active

I = 14

This group starts with stable isotope Se^{82} and ends with Sn^{114} β^--active isotopes at Br^{84} and Nb^{96} are expected Besides, a stable Sr^{90} is expected Nier (1938) looked for the isotope and has found that if it exists its abundance is less than 3×10^{-5}

I = 15

The first stable nucleus of this group is at Ag^{109} and the last one at Sn^{115} The nucleus Pd^{107} may be also stable Br^{85}, Rb^{89}, Sr^{91}, Y^{93} and Nb^{97} may be β^--active

Masurium

The element '43' Masurium has not yet been satisfactorily identified Let us see what prediction can be made about it It is expected to have isotopes of the following atomic weights

94	95	96	97	98	99	100	101	102	103
+	+	+−	St	+−	St	+−	−	−	−

The two stable isotopes are expected to have the masses 97 and 99 Of these 99 is expected to be more abundant $_{43}Ma^{99}$, though not yet observed on the earth, has been detected by an indirect method by Abelson (1939*b*) He observed that Mo^{99}, which is β^--active (period 64 hrs), has, besides, a branch activity, and one-fifth of Mo^{99} is converted to $_{43}Ma^{99}$ which emits a γ-ray and lapses to a stable isotope The γ-ray is internally converted, which expels an electron from the K-shell, and $K\alpha$-line of Ma is emitted This has been detected by Abelson

I = 16 (See Chart 2)

The first stable isotope is at Zr^{96} and the last one so far detected is Xe^{124} The following radioactive nuclei may be looked for —

Nb^{98}	Ma^{102}	Rh^{106}	Sb^{118}	I^{122}
−	−	−	+	+

I = 17

There are only three stable nuclei Cd^{113}, In^{115} and Sn^{117} in this group Sb^{119} is not yet known It may be either stable or β^+-active Ma^{103} and Rh^{107} may be β^--active

I = 18

This group starts with Pd^{110} and is continued up to Ba^{130} Cs^{128} may be β^+-active

I = 19

The stable isotopes in this group are Sn^{119}, Sb^{121} and Te^{123} After these we have neither stable nor radioactive nuclei in this group I^{125} may be either stable or β^+-active, so is Xe^{127}

I = 20

The group starts with the stable nucleus Cd^{116} and is continued up to Sm^{144} There is a notable absentee amongst stable nuclei at Nd^{140} Radioactive nuclei are expected at

In^{118}	Cs^{130}	La^{134}	Pr^{138}	${}_{61}X^{192}$
−	+−	+	+	+

I = 21

We have got four stable nuclei in this group from Sb^{123} to Xe^{129} It will be interesting to look for nuclei further beyond at Cs^{131}, Ba^{133}, La^{135} and Ce^{137} I^{119} may be β^--active

I = 22

The first stable isotope is Sn^{122} and the stable series terminates at the stable isotope Nd^{142} Radioactive nuclei can be looked for at Cs^{132}, (+ −), La^{136} (+ −)

I = 23

The first stable nucleus in this group is Xe^{131} and the last one is Sm^{147} La^{137} is a notable absentee and Ce^{139} is anomalous According to our rule this ought to be stable As a matter of fact cerium shows anomaly in the next group I = 25 and Ce^{139} as well as Ce^{141}, which are shown to be β^+- and β^--active respectively, ought to be stable according to our rule The gap at ${}_{61}X^{145}$ is still to be filled up

I = 24

This group shows the first stable nucleus at Sn^{124} and is continued up to Gd^{152} Sb^{126} ought to be β^--active Sm^{148} is α-active This is indicated by the double arrow which shows that after the emission of α-ray it is transformed into Nd^{144} According to our classification α-active substances are to be classed with stable nuclei

I = 25

The first stable nucleus is at Ba^{137} and excepting for the anomaly at Ce^{141} this group is continued up to Eu^{151} Xe^{133} and Cs^{135} may be either stable or β^--active Pr^{143} ought to be a stable isotope, so should also be ${}_{61}X^{147}$ Gd^{153} may be stable or β^+-active

I = 26

The first stable nucleus is at Te^{130} and the last is at Er^{162} One may look for the radioactive nuclei at

I^{132}	Cs^{136}	Pr^{144}	${}_{61}X^{148}$	Tb^{156}	Ho^{160}
−	−	−	+	+	+

$I = 27$

This contains only two successive stable elements at Eu^{153} and [illegible]. The next element Tb^{157} is also probably stable This group is flanked [illegible] both sides by radioactive nuclei which start from Sb^{129} Search may be made for other radioactive nuclei at

I^{133}	Xe^{135}	Cs^{137}	La^{141}	Ce^{143}	Pr^{145}	${}_{61}X^{149}$	Tb^{157}	Ho^{161}	Er^{163}	Tu^{165}
−	−	−	−	−	−	−	+	+	+	+

$I = 28$

This group starts with the stable nucleus Xe^{136} and we should have stable nuclei at Ba^{140} and Ce^{144} Others, which according to our rule should occur, are present up to Yb^{168} We should expect the following radioactive nuclei —

Cs^{138}	La^{142}	Pr^{146}	${}_{61}X^{150}$	Ho^{162}	Tu^{166}	Lu^{170} etc
−	−	−	−	+	+	+

$I = 29$

We have three successive stable nuclei at Gd^{157}, Tb^{159}, Dy^{161} Eu^{155} and Ho^{163} may be either stable or radioactive The following radioactive nuclei may be looked for —

${}_{61}X^{151}$	Eu^{155}	Ho^{163}	Tu^{167}	Lu^{171} etc
−	−	+	+	+

$I = 30$

The group starts with the stable nucleus Nd^{150} and is continued up to Hf^{174} W^{178} may be a stable isotope of tungsten The following radioactive nuclei are expected —

${}_{61}X^{152}$	Eu^{156}	Tu^{168}	Lu^{172}	Ta^{176}	Re^{180}
−	−	−+	+	+	+

Element 61

The discovery of element '61' has been claimed and disputed It is possible to make predictions regarding its number of stable isotopes, their abundance, and radioactive-isotopes The chart shows that we may expect isotopes having the mass-numbers —

144	145	146	147	148	149	150	151	152
+	St	+−	St	+−	−	+−	−	−

The two stable isotopes with $A = 145$, 147 will have probably the same order of abundance

$I = 31$

We have got five successive stable nuclei, viz , Dy^{163}, Ho^{165}, Er^{167}, Tu^{169}, Yb^{171} They are flanked by a certain number of radioactive nuclei Search may be made for

${}_{61}X^{153}$	Sm^{155}	Eu^{157}	Tb^{161}	Lu^{173}	Hf^{175}	Ta^{177}	W^{179}
−	−	−	− or St ?	+	+	+	+

I = 32

The series starts with the stable nucleus Gd^{160} and terminates at Os^{184} Search may be made for the following radioactive nuclei —

Tb^{162}	Lu^{174}	Ta^{178}	Re^{182}
$-$	$-\,+$	$+$	$+$

I = 33

We have three successive stable nuclei at Yb^{173}, Lu^{175} and Hf^{177} Tu^{171} and Ta^{179} may also probably be stable Search may be made for the following radioactive elements —

Ho^{167}	W^{181}	Re^{183}	Os^{185} etc
$-$	$+$	$+$	$+$

It may be mentioned here, as a proof of the usefulness of the table, that it makes Lu^{175} stable and probably the most abundant isotope But this nucleus is mentioned as β^{-}-active in the Tables published by Gregoire (1938*b*) Mattauch and Lichtblau (1939) have subsequently shown that there is an isotope at Lu^{176} with abundance of 2 5% and it has been shown by Libby (1939) that it is Lu^{176} which is β^{-}-active with the unusually long life of 10^{10} yrs and not Lu^{175} Lu^{176} is thus just like long-lived K^{40} and Rb^{87}

I = 34

This series starts with the stable nucleus Er^{170} and terminates at the stable nucleus Os^{186} The following radioactive nuclei may be looked for —

Tu^{172}	Re^{184}
$-$	$-\,+$

I = 35

There are five successive stable isotopes beginning from Hf^{179} up to Os^{187} They are flanked on the left by two β^{-}-active nuclei and the following may be looked for —

Tu^{173}	Lu^{177}	Ir^{189}	Pt^{191}
$-$	$-$ St ?	$+$	$+$

I = 36

The series starts with the stable isotope Yb^{176} and ends with Hg^{196} Search may be made for

Lu^{178}	Ir^{190}	Au^{194}	Tl^{198}
$-$	$+$	$+$	$+$

I = 37

There are three successive stable nuclei at Re^{187}, Os^{189} and Ir^{191}, flanked as usual on the left by the β^{-}-active and on the right by β^{+}-active nuclei Search may be made for

Ta^{183}	Au^{195}
$-$	$+$

$I = 38$

This series starts with W^{186} and ends with Hg^{198} Au^{196} is shown as a β^--active nucleus with two periods 4 days and 13 hours

$I = 39$

This series has four successive stable nuclei from Ir^{193} to Hg^{199} There may be more stable nuclei to the right, *e g* at Tl^{201}

$I = 40$

This series starts with the stable nucleus Os^{192} and ends with Pb^{204} Tl^{202} may be β^+-active

$I = 41$

We have two successive stable nuclei, Hg^{201} and Tl^{203} Pb^{205} may be a stable isotope On the left side we have the β^--active nuclei Au^{199}, Pt^{197} and Os^{193}, but on the right side no representative has yet been obtained We may have Ir^{195} (β^--active) and Bi^{207} and Po^{209} (β^+-active)

$I = 42$

From this series we enter the region of natural radioactivity, the α-emitting nuclei are treated as stable for our purpose The rule of alternation is obeyed in this series and we have stable nuclei at Pt^{198}, Hg^{202}, Pb^{206} and Po^{210}, the last one being α-active Au^{200} ought to be β^--active and Bi^{208} ought to be β^+-active These have not yet been found

$I = 43$

This series also obeys the laws stated, as we have successive stable isotopes at Tl^{205}, Pb^{207}, Bi^{209} and Po^{211} (α-active) The group is flanked on the left by β^--active nuclei in which Au^{201} is an absentee On the right, β^+-active nuclei may be expected, such as ${}_{85}X^{213}$ and Rn^{215}

$I = 44$

Here also the rule of alternation is followed from Hg^{204} up to Po^{212} (α-active) No β-active nuclei on the left or right have yet been found

$I = 45$

We have three β^--active nuclei and only one 'stable' (α-active) isotope at Bi^{211} Both Po^{213} and ${}_{85}X^{215}$ may be either stable or α-active nuclei

$I = 46$

Only four isotopes are present which follow the rule, excepting Pb^{210} which is an anomaly This nucleus is actually β^--active but ought to be stable or α-active according to our scheme Rn^{218} may be stable

$I = 47$

We have 'stable' nuclei at Po^{215}, Rn^{219}, Ra^{223} and Th^{227}, all being α-active If the odd number rule is valid then probably ${}_{85}X^{217}$, ${}_{87}X^{221}$ and Ac^{225} should also be 'stable' or α-active

I = 48

In this series Pb^{212} (Th B) should be stable, but actually it is β^--active. Bi^{214} (Ra C) should be β^--active but this actually emits, as is well known, both α- and β-rays. Apart from these two anomalies the other nuclei in this series follow the stability rule. These are Po^{216}, Rn^{220}, Ra^{224} and Th^{228}, all being α-active. We should expect $_{85}\mathrm{X}^{218}$, $_{87}\mathrm{X}^{222}$ and Ac^{226} to be all β^--active.

I = 49

This group is very small having only two stable isotopes at Th^{229} (which is doubtful) and Pa^{231} (which is α-active). U^{233}, if it could be obtained, would probably be α-active.

I = 50

Here also we have an exception to the rule in Pb^{214} (Ra B). It ought to emit α-particle, but actually it emits β-rays passing to Ra C. Other nuclei follow the rule. These are Po^{218}, Rn^{222}, Ra^{226}, Th^{230} and U^{234}, all being α-active. We ought to have β^--active nuclei at Bi^{216}, $_{85}\mathrm{X}^{220}$ and $_{87}\mathrm{X}^{224}$. Ac^{228} is found to be β^--active and Pa^{232} may be β^+-active.

I = 51

There is a single stable nucleus U^{235} flanked by three β^--active nuclei on the left. $_{93}\mathrm{X}^{237}$, according to these rules, may be 'stable', i.e. α-active. It is now well known that U^{235} forms about 0.7% of the most abundant isotope U^{238}.

I = 52

Here also we start with an anomaly at Ra^{228} which instead of being α active is β^--active. The other two nuclei in this group are Th^{232} which is α-active as it ought to be, and Pa^{234} which is β^--active. U^{236} ought to be stable (or α-active). $_{93}\mathrm{X}^{238}$ ought to be β^+-active.

I = 53

There are only three nuclei in this group of which the first two, e.g., Ra^{229} and Th^{233} are β^--active and $_{93}\mathrm{X}^{239}$ is probably stable or α-active. U^{237} may be either α- or β-active. Ac^{231} and Pa^{235} will probably be β^--active.

I = 54

In this group the nucleus Th^{234} is an anomaly, because according to the rules it should be α-active, but actually it is β^--active. Pa^{236} ought to be β^--active.

Element 85—Radio-Iodine

Element 85, still undiscovered, is expected to have isotopes of the following mass-numbers —

212	213	214	215	216	217	218	219	220
—	St (?)	—	St. (?)	—	St or α-	— or α-	—	—

The stable isotope of element 85 should have an atomic mass of 217

Element 87—*Radio-Caesium*

This element is expected to have isotopes of the following mass-numbers —

221	222	223	224
St or α·	—	—	—

So it appears to have only one stable isotope of mass-number 221.

Fission of Uranium and Thorium

After a certain amount of progress had been made with this paper, we received the September (1939) number of the *Physical Review*, containing a paper by Bohr and Wheeler (1939) on the 'Mechanism of Nuclear Fission' In this paper, the mechanism of nuclear fission is explained by using a (I)/A-diagram (Fig 8, p 445) which is very nearly identical with the one used here As mentioned already, only a part of the diagram from Bi^{98} to Sm^{140} is shown, and no other use is made of it, except to illustrate the mechanism of fission

A few points regarding fission can be elucidated by means of our chart It has been now proved that the effect of bombarding U or Th-nuclei with neutrons is probably (1) to release a number of neutrons, estimates vary from 2 to 6 (see Zinn and Szilard, 1939), (2) to split up the remaining nucleus into almost two equal halves, which leave each other with energy of about 200 Mev The energy of splitting can be calculated from theoretical considerations of the energy-formation of nuclei, and is found to be in accordance with experimental observations

In some cases, the products of fission and the products of successive disintegrations have been correctly identified, in other cases all the links have not been satisfactorily traced We give below in Table I a summary of the results so far obtained by different observers, showing the successive series which have been observed

The tables have been compiled from recent works, particularly those due to Hahn and his co-workers (1939), and Abelson (1939*a*) We may add some notes regarding the establishment of each series of successive products, and identification of the mass of the nucleus, which is indicated at the top of each column

The first series (second column of Table I)

$$\begin{array}{ccccc} {}_{51}Sb^{127} & \rightarrow \beta^- & {}_{52}Te^{127} & \rightarrow \beta^- & {}_{53}I^{127} \\ 80h & & 10h & & \text{stable} \end{array}$$

has been cleared up by Abelson, and its mass, 127, was identified from the observation that a 10*h*-Te isomer was already discovered by Seaborg, Livingood, and Kennedy (1937) It should terminate with stable I^{127} The fission nuclei are indicated by the symbol $\underset{\downarrow}{\ominus}$ in the Chart The nuclei under mass numbers against which there are query marks have not been shown in the Chart

TABLE I

Products of Fission of Uranium

Mass / Nuclei	127	129	131	133?	135?	137?	139	141?	143?
$_{50}$Sn									
$_{51}$Sb	*80h*	*4 2h*		*5m*	< *10m*	< *10m*			
$_{52}$Te	*90d* *10h*	*30d* *70m*	*30h* *25m*	*77h*	*43m*	*60m*			
$_{53}$I	I^{127} stable	*18 5h*	*8d*	*2 4h*	*54m*	*22h*			
$_{54}$Xe		Xe^{129} stable	Xe^{131} stable	st or —(?)	—	—		*15m*	
$_{55}$Cs				Cs−^{133} stable	st or—	—	*6m*	*33m*	
$_{56}$Ba					Ba^{135} stable	Ba^{137} stable	*86m*	*300h*	*14m*
$_{57}$La							La^{139} stable	*36h*	*2 5h*
$_{58}$Ce								Ce^{141*} stable?	—
$_{59}$Pr									Pr^{143} stable
$_{60}$Nd									

* *Vide* remarks, page 55

The mass of the second series (A = 129) was identified from the 70*m* (1 *h*)-Te discovered by Seaborg *et al* It should end in Xe^{129} (stable—26%)

The mass of the third series (A = 131) was identified from the 8*d*-I, discovered by Seaborg *et al* It should end in Xe^{131} (stable—2 2%)

The identification of the masses of the three remaining series is far from clear, but they cannot have the even masses, 132, 134, 136, as suggested by Abelson (1939*a*), for according to our chart (*vide* mass-lines 132, 134, 136), I^{132}, Te^{134} and I^{136} should be *stable* One has merely to go up along the mass-lines 132, 134, 136 and it can at once be seen that the points I^{132}, Te^{134}, I^{136} would be stable according to the rules formulated by us

These three unidentified series should have therefore the odd mass-numbers 133, 135, 137 respectively, but it is of course not possible to say which number refers to which group

X^{133}-group should end in Cs^{133}, *i e* we should have in addition a β^--emitting Xe^{133} in this group There is just a chance that Xe^{133} may be stable

X^{135}-group should end in Ba^{135}, or Cs^{135} if the latter is stable In any case, we should have a Xe^{135}, β^--emitting

X^{137}-group should end in Ba^{137} Hence this group should show a β-emitting Cs^{137} and a β^--emitting Xe^{137}

The end product of X^{139} has been definitely identified by Hahn *et al* (1939) with La^{139}

The masses of the other two groups are not yet definite But they cannot be even for the same reason as in the case of $X^{133,\ 135,\ 137}$ but odd They have probably the mass-numbers 141 and 143

The group X^{141} should end in Ce^{141}, which as remarked already should be a stable isotope of Ce

The group X^{143} should end in Pr^{143}, *i e* it should have β^--emitting Ce^{143}

We have thus shown that according to Hahn *et al*, and Abelson, one of the immediate products of fission of uranium may be any odd mass from 127 to 143, 9 in number These contain too large a proportion of neutrons, and therefore undergo successive β^--transformations till they end in stable nuclei which have invariably odd mass numbers The highest number of β^--transformation so far detected is four (for X^{141})

Since the starting nucleus was either U^{239} or U^{235}, and probably two neutrons are emitted before fission, the other component of fission would be a nucleus with an even mass For example, the other component of the fission process which gives rise to ${}_{54}X^{143}$ should be ${}_{38}X^{90}$ The results on this side are rather confusing, and the different series have not been completely worked out Only the following series appear to have been worked out fully —

$$\begin{array}{ccccccc} {}_{35}Br^{88} & \rightarrow & {}_{36}Kr^{88} & \rightarrow & {}_{37}Rb^{88} & \rightarrow & {}_{38}Sr^{88} \\ 35m & & 3h\ (?) & & 17m & & \text{Stable} \end{array}$$

This is based on the identification of ${}_{36}Kr^{88}$, which is, however, doubtful (Langsdorff, 1939)

SUMMARY

A chart has been drawn with A, the mass-number as abscissa, I, the isotope number which is defined as the excess of the number of neutrons over protons as ordinate, and Z-lines, at 45° to the abscissa or ordinate In this chart, all nuclei, stable as well as radioactive, have been represented with their abundance (for stable nuclei) and half-lives The chart enables one to form a complete picture of all nuclei so far known, as well as of the nuclear processes Rules of stability have been noticed, in the case of nuclei with even mass-number, these have been partly foreshadowed by Bethe and Bacher, the rules for stability of odd nuclei which are noted here are believed to be new A large number of predictions have been made regarding the occurrence of rare stable nuclei, and of radioactive nuclei In the case of elements still undiscovered, Nos 43, 61, 85, 87, predictions have been made regarding the

number of isotopes and of the most stable varieties A number of anomalies in the present list of stable elements has been pointed out which ought to be cleared up The mass-numbers of the U-fission product series to which Abelson assigned the values 132, 134, 136 have been shown to be untenable The correct mass-numbers appear to be 131, 133, 135 respectively Further, two series have been shown to possess the mass-numbers 141 and 143 respectively

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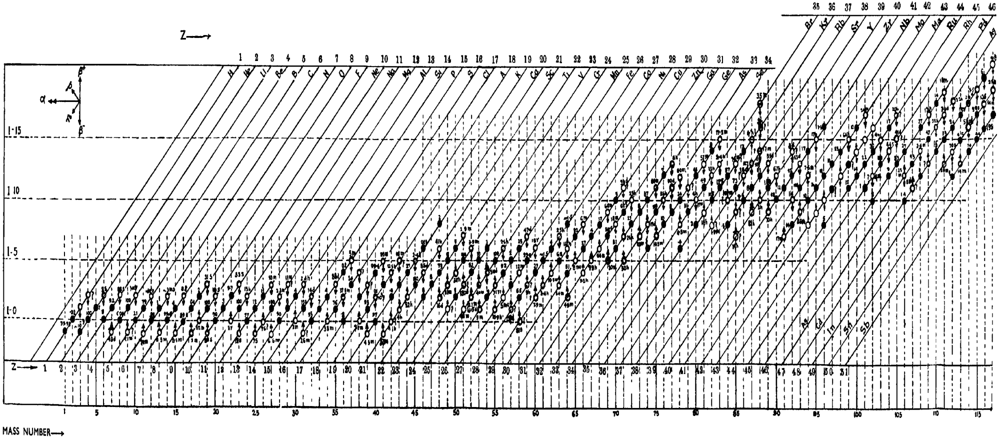
CHART 1


Z ⟶
Z ⟶
MASS NUMBER ⟶
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α
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H He Li Be B C N O F Ne Na Mg Al Si P S Cl A K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se
Br Kr Rb Sr Y Zr Nb Mo Ma Ru Rh Pd Ag
Ag Cd In Sn Sb
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34
35 36 37 38 39 40 41 42 43 44 45 46
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51
1 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115

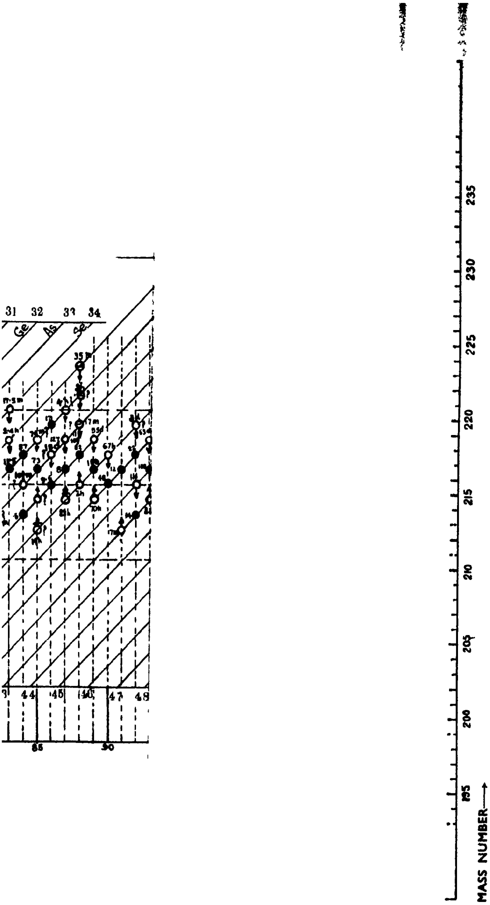
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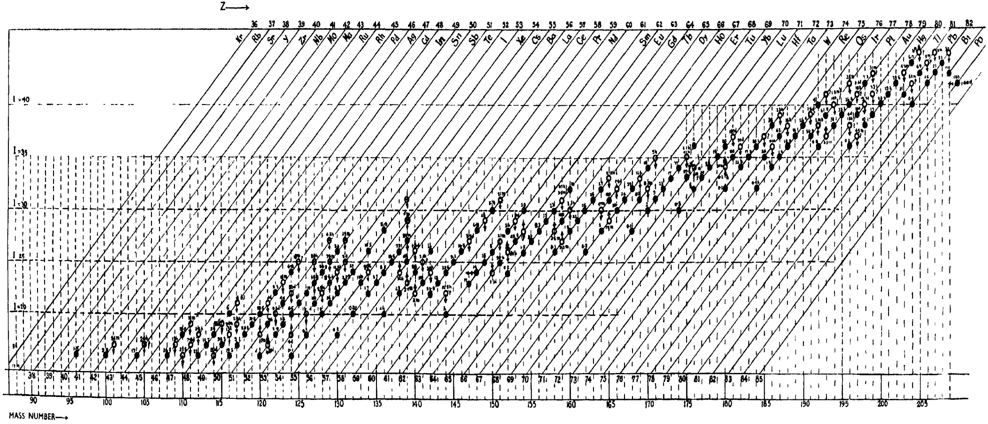
CHART 2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Kr
Rb
Sr
Y
Zr
Nb
Mo
Ma
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Xe
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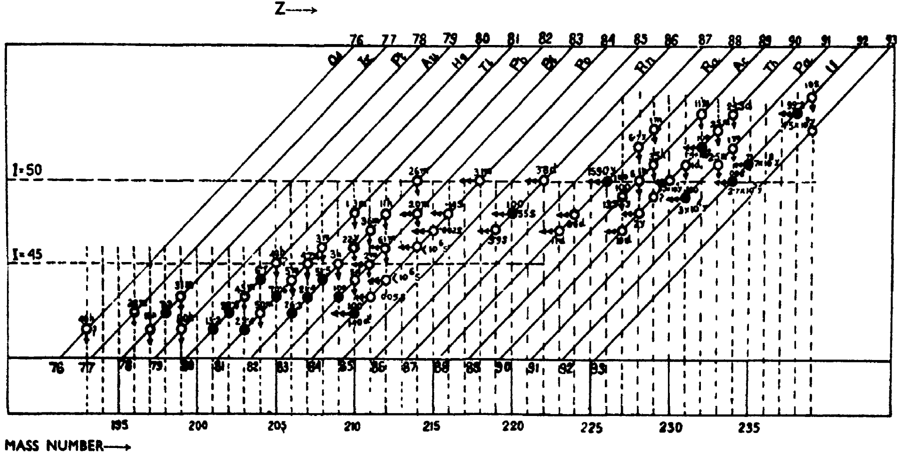
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THE SECOND MAXIMUM OF THE ROSSI CURVE

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(Communicated by Prof M N Saha, F R S)

(*Read March 11, 1940*)

Introduction

During recent years great progress has been made in understanding the phenomenon of production of showers by high-energy electrons and positrons It is known that such an electron (or positron), during its passage through matter, loses energy partly by ionization and partly by radiation For every material there is a critical energy (E_c) at which the energy losses due to radiation and ionization are equal If the energy of the particle is above the critical energy, the energy-loss due to radiation exceeds that due to ionization, while the reverse is true if the energy of the incident particle is less than E_c This critical energy for lead is about ten million electron volts A cosmic ray electron, whose energy is generally much higher than this amount, will at first lose its energy mainly by radiation during its passage through lead The electron then radiates a few hard quanta which proceed in almost the same direction as the original electron and in their turn lose energy by creating pairs of positive and negative electrons Each quantum gives rise to one pair of electrons which share the total energy of the quantum Hence, if we had started with one primary electron of energy E_0 incident on a sheet of matter, after a small thickness is traversed, we are left with several electrons of both signs which have energies comparable to E_0

Each of these electrons continues the process of generation of fresh quanta and ultimately of pairs of electrons The size of the shower, *i e* the number of secondaries produced by the primary electron, increases and the energy of the shower electrons decreases as more and more matter is traversed Finally, the critical energy of the material is reached when the energy-loss due to ionization becomes equal to that due to radiation The ionization-loss becomes still more effective as the energy of the electron is further reduced No multiplication therefore takes place and the electron is ultimately stopped due to its energy being completely lost by ionization

This cascade theory of shower formation has been worked out in detail by Bhabha and Heitler (1937) as well as by Carlson and Oppenheimer (1937) Their theoretical predictions are confirmed in a very striking manner by the cloud chamber photographs of Fussell (1937), Trumpy (1938) and Street

[Published April 12th, 1940.

1939) In these photographs the successive stages of shower formation by radiation and pair-formation are clearly visible From the work of Fussell it is also evident that the majority of the showers at the sea level are produced by the cascade process

In order to study the showers released from a sheet of lead by the incident cosmic rays, Rossi (1934) employed a system of three counters arranged in such a way that the same particle cannot pass through all of them If these counters are activated simultaneously a coincidence is recorded which indicates in general the release of two or more ionizing particles from lead Rossi found that with his arrangement the number of coincidences increased with the thickness of lead used and that this number reached a maximum at a thickness of about 1 6 cms of lead Since the work of Rossi a great variety of counter and radiator arrangements have been used in order to study in detail the nature of the showers released from thin sheets (Froman and Stearns, 1938) As a result of these investigations it is now well established that the formation of showers under small thickness of matter and also the first maximum of the Rossi curve can be well explained by the cascade theory by assuming that they are caused by the soft component of the cosmic rays

The showers under great masses of matter have been investigated by Follett and Crawshaw (1936), Ehmert (1937) and Morgan and Nielson (1937) As mentioned before the intensity of the cosmic ray showers in lead rises to a prominent maximum at about 1 6 cms of lead, after which the shower, intensity falls rapidly with increasing thickness of the radiator Beyond ten cms of lead the rate of diminution becomes very small and the transition curve finally extends into a long tail with very little slope Ackemann (1935), Hummel (1934), Drigo (1934) and Clay, Gemert and Wiersma (1936) showed that there is a second rise in the coincidence curve at a thickness much beyond that corresponding to the first maximum They found that as the radiator thickness is increased, the shower frequency reaches a second maximum between 16 to 20 cms of lead This is known as the second maximum of the Rossi curve after which the shower frequency again diminishes Bothe and Schmeisser (1938) made a detailed study of this second maximum and came to the conclusion that this becomes more prominent as the angle at which the shower is observed is reduced At angles greater than ten degrees the second maximum is hardly noticeable, while at four degrees it is as prominent as the first Bothe accounted for the failure of some of the early observers to detect a prominent second maximum to be due to their using wide angles

By conducting the experiment under open sky and also in the cellar Bothe showed that the second maximum is produced by the penetrating component of the cosmic rays, a fact which is also evident from its position. Theoretically the exact mechanism by which mesotrons give rise to this second shower maximum is not very clear A mesotron can initiate showers in two distinct types of processes. The first is the ionization shower postulated by Bhabha (1938). In this process a mesotron is supposed to knock out an extra-nuclear electron to which it gives less than half its kinetic energy The knocked out electron subsequently produces an electron shower in the usual cascade process Bhabha (1938) estimated that due to this process in lead mesotrons of energy of 10^{10} e v will be associated with soft electrons to the extent of fifteen per cent According to Hopkins, Nielsen and Nordheim (1939) and Lovell (1939) the majority of the showers under thick layers of matter are fully accounted for by the Bhabha ionization process Difficulties, however, arise as soon as attempts are made to explain the production of the second maximum of the Rossi curve by the Bhabha ionization process A characteristic of these ionization showers will be that the primary mesotron will come out of the radiator associated with the shower particles which will be ordinary electrons From the position of the second maximum and also the rate of absorption of the shower particles it appears that the shower particles in this case are not ordinary electrons but mesotrons

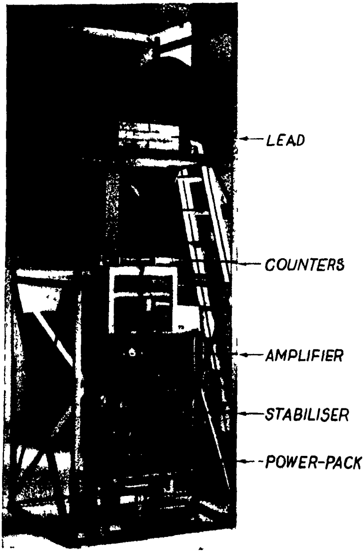
The other alternative in which mesotron showers may be produced is the multiple emission process, in which a heavy electron is absorbed or scattered by the nucleus and several heavy electrons are produced The showers generated in this way have been investigated theoretically by Heisenberg (1939), Heitler (1938) and Wentzel (1938) But the occurrence of such close angle showers ($<10°$) as found by Bothe and Schmeisser cannot be explained on this theory unless some arbitrary cutting principles are introduced

It will be evident from the above that the exact mode of origin of the second maximum is not very clear It may be that the showers of both kinds are present in this maximum (Ehmert, 1939) Apart from these theoretical uncertainties great doubt has been thrown on the presence of this maximum by the recent work of Morgan, Nielsen and Nielsen (1939) They investigated showers under great masses of iron using four-fold coincidences for recording the showers The showers at both 7° and 38° were recorded but no second maximum could be found in the shower curve, even though the radiator thickness was increased up to 300 gms /cm ^{2} As the four-fold coincidence method should be more sensitive to the showers from the top, the authors conclude that the second maximum found by Bothe and Schmeisser is due to background effect It is, however, not clear why the background effect should occur only at a particular lead thickness

On account of these theoretical and experimental uncertainties present in the second maximum of the Rossi curve it was decided to carry out a series of investigations on the second maximum using different experimental arrangements The present paper contains an account of the preliminary work in which we have repeated Bothe's experiment with three-fold coincidence arrangement

EXPERIMENTAL ARRANGEMENT.

The cosmic ray shower apparatus used in this experiment is shown in fig. 1 It consists of a massive iron frame capable of supporting a ton of lead above the counter assembly The lead radiator, more than 20 cms thick, which was formed with bricks piled upon one another can be seen at the top of fig 1 The radiator covered a total surface area of 40×40 cm ^{2}



COSMIC RAY SHOWER APPARATUS

FIG 1.

The counter assembly consisting of four counters, the amplifier with the thyratron recorder, the high voltage stabilizer for supplying voltage for the counters and the power-pack for the amplifier can be seen in fig 1 The apparatus was made portable and suitable for outdoor work The amplifier for recording four-fold coincidences was of Barasch (1934) type using a discriminator and a final pulse equalizing valve The high voltage stabilizer using Street and Johnson's (1932) circuit was capable of supplying a high tension up to 3000 volts. Fig. 2 represents the arrangement of the counters.

Four counters were arranged at the corners of a trapezium below the lead radiator which was 77 cms above the two lower counters, these subtended an angle of about 6° at the middle point of the lower surface of the radiator

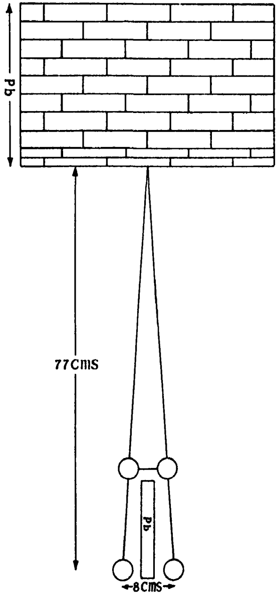


Fig 2

Only three-fold coincidences were recorded with the two upper counters connected in parallel By this arrangement at least two shower particles were necessary to cause a coincidence An intermediate sheet of lead 1·5 cm thick was placed between the lower counters so as to stop the spurious coincidences caused by the electrons released from the counter walls passing from one into another There was no absorber between the upper and lower counters.

Most of the measurements were made with brass counters 0·7 mm. thick, 2·5 cms wide and having a working length of 20 cms The counters were sealed in pyrex tube 0·4 gms /cm ^{2} thick In order to cause a coincidence a cosmic ray particle had to traverse a total thickness of 3 75 gms /cm ^{2} including a piece of wood supporting the upper counters From the calculations of Bethe and Heitler (1934) it was estimated that the cosmic ray particles causing the coincidences had energies exceeding 10 million electron volts

RESULTS

The following table indicates the results obtained with different thicknesses of the lead radiator placed on the top of the iron plate, quarter inch thick This thickness of iron is equivalent to a thickness of about 0·2 cms of lead, according to Bhabha's theories This constant thickness of 0·2 cms has been added to the actual lead thickness in order to get the figures given in column (1) under the head 'total thickness of the lead radiator'.

As the number of coincidences per hour was small, each reading had to be extended over a great length of time in order to count a sufficient number of coincidences, to reduce the statistical errors The total number of coincidences counted is indicated in column (3), while the total time involved in each reading is given in column (2) The rate of coincidences per hour has been indicated in the last column with the probable error 68 $\sqrt{N}/T$ where N = total number of coincidences and T the total time of counting No correction has been made for the accidental coincidences, calculation showed that they would be about 0 85 per hour The results are shown plotted in fig 3 where the probable error in determination has been indicated by vertical lines

TABLE I

Total thickness of the Pb radiator in cms.	Total time of counting in minutes	Total number of coincidences counted	Coincidence per hour
2	498	68	8 2± 67
1 2	724	122	10 5± 64
2 2	656	104	9 5± 63
4 7	1139	147	7 7± 44
7 2	1550	147	5 7± 32
9 7	704	59	5 0± 44
12·2	786	64	4 9± 42
14 7	1075	74	4 1± 32
17·2	1002	91	5 5± 39
19 7	1236	129	6·3± 38
22 2	541	47	5·2± 52

From the curve shown in fig. 3 it will be evident that the coincidence curve has two prominent maxima of comparable intensities The second maximum occurs at a thickness of lead of about 18·5 cm which is slightly greater than that found by Schmeisser and Bothe (16·5 cm.) The intensity of the first maximum is much reduced as only close angle showers were observed and the experiment was carried out under one layer concrete roof of thickness

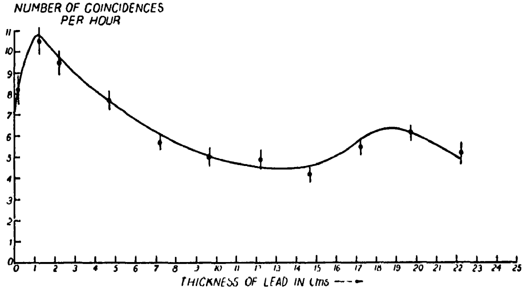


FIG 3

20 cms approximately This cuts off some of the softer components of the incident cosmic radiation The second maximum is, however, unaffected by such small thickness of matter The occurrence of the second maximum at 18 5 cms is in very good agreement with the calculations of Ehmert (1939) based on the absorption coefficient of the shower particles

The first maximum occurs at 1 3 cm of Pb thickness which is slightly less than the usually accepted value of 1 6 cm No great care was, however, taken to determine its position very accurately, as the chief interest of the experiment was to test the presence of the second maximum if any It will be apparent from fig 3 that there are many coincidences even with no Pb radiator placed above the counters These are due to showers from air, roof, walls, etc which are partially absorbed by increasing the thickness of the Pb radiator The second part of this background effect is not affected by placing Pb over the counters As found by Bothe and Schmeisser it is not possible to avoid completely this background effect However, the presence of two maxima in the shower curve is clearly proved by the results of the present experiment

The experiment was carried out in the Cosmic Ray Research section of the University College of Science at Calcutta It is with great pleasure the writer acknowledges his grateful thanks to Prof M N Saha, D Sc , F R S , for his kind interest and encouragement in this line of research My thanks are also due to Dr S C Sirkar and Mr P C Bhattacharya for helpful discussions.

SUMMARY

Cosmic ray showers from lead have been investigated with three-fold coincidence arrangement up to a total thickness of 22 cms of lead The minimum angle subtended by the shower particles at the lower surface of the radiator was 6° With this arrangement the shower curve shows two prominent maxima at 1 3 cms and 18 5 cms of lead

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A CONTRIBUTION TO THE MORPHOLOGY AND CYTOLOGY OF *CARTHAMUS TINCTORIUS* LINN

By I Banerji, *Department of Botany, Calcutta University*

(Communicated by Prof S P Agharkar, Ph D , F L S)

(*Read January 2, 1940*)

Carthamus tinctorius, commonly known as 'Safflower', is a crop plant of great economic importance It is widely cultivated in India both as an oil seed crop, and for the reddish dye in the flowers (*Carthamin*) The dye is found in the florets and these are collected at frequent intervals after the setting of the seeds The oil extracted from the seeds is known as 'Kusum' oil, and is supposed to have good drying properties It is grown in India chiefly as a '*Rabi*' crop

The plant belongs to the tribe Cynareæ of the family Compositæ An account of the flowering, pollination, natural cross-fertilisation and the isolation and description of 24 unit species has already been given by Howard, Howard and Khan (9) The chromosome number of the plant was first recorded by Gregory (7) who found the diploid number to be 20 Later, Patel and Narayana (15) who worked on Pusa types found the monoploid and diploid numbers to be twelve and twenty-four respectively This has been confirmed by Gregory (6) for the Pusa types, and he is of opinion that the variation found in the chromosome number was due to his having worked previously with Coimbatore types—which might be distinct karyotypes Gregory (7) has also worked out the process of somatic mitosis in this plant, and has demonstrated the chromonematic structure of the chromosomes No other literature on *Carthamus tinctorius*, besides those mentioned above, has been noted by the present writer

A considerable amount of morphological and cytological work has, however, been done on the family Compositæ Schnarf (16) and lately Bhargava (1) have summarized the literature and it need not be repeated here As no reference was found on *Carthamus tinctorius*, it was thought desirable to take up the investigation of which this paper gives an account

MATERIAL AND METHODS

The material was collected from plants grown in the University College experimental garden from seeds obtained locally The cultures were quite uniform and aberrant forms were weeded out Capitula of various sizes were fixed Before fixation the involucral bracts were removed and the buds trimmed In some cases it was necessary to cut the heads into three or four

VOL. VI—No. 1. [Published April 12th, 1940.

parts and remove the upper portions of the flowers. Allen's modified Bouin's fluid, Licent's fluid and Nawaschin's fluids were chiefly used for fixation The first and the last fixative gave good results, but Licent's fluid was found to be better suited for the study of embryology The material was dehydrated and cleared in the usual way. Sections were cut 6 to 16μ thick depending on the stage required for study Heidenhain's iron-alum Hæmatoxylin and Newton's Iodine Gentian Violet stain were chiefly used

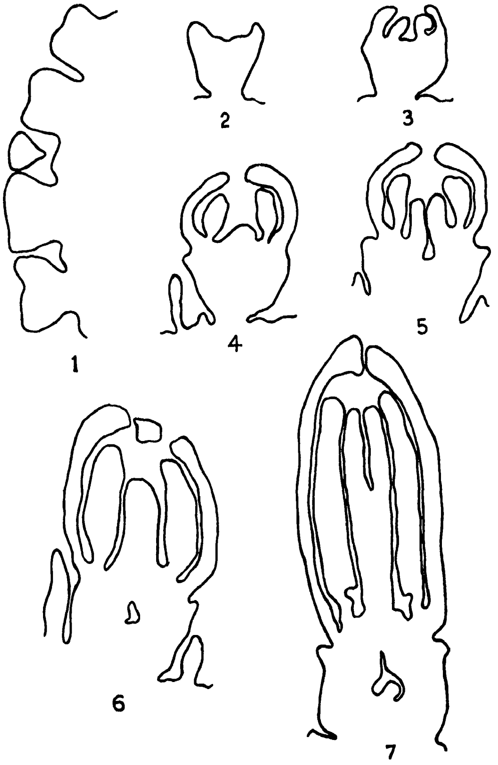
OBSERVATIONS

(*a*) *The Development of the flower* —Before the differentiation of the florets the floral axis is convex in outline and is covered by the overlapping bracts The primordia of the individual florets soon arise in large numbers as minute protuberances of the thalamus and are at first convex in outline From the edges of the convex papillate processes a number of primordia very soon grow actively and as a result the central region becomes concave in outline (Text-figs 1 and 2) The outgrowths from the sides, which are five in number (as seen in transverse section), curve inwards particularly at their tips and form an effective covering in the early stages of the development of the flower These are the petals The primordia of the stamens are seen next, followed immediately by those of the sepals (Text-figs 3 and 4) The staminal primordia, which are five in number, grow rapidly and soon the anther lobes become differentiated The calyx primordia on the other hand remain as mere angular projections and do not develop any further (Text-figs 4 and 5) The last floral whorl to appear is that of the two carpels which originate on the thalamus close to the inner side of the stamens (Text-fig 5) They remain free in the early stages of their development but very soon cohere and form the style (Text-fig 6) At the top, however, they remain free (Text-fig 7) A flask-shaped cavity is seen at the base of the carpels, where the ovule originates as a minute protuberance (Text-fig 7)

It has been suggested that in many Compositæ the style is spirally coiled at the base and by its elongation at maturity, it brushes against the anthers and thus secures self-pollination Careful examination of the present material showed no such arrangement As stated before, the tip of the style is divided and clothed by unicellular hairs Pollination is brought about by the sigmatic thrust which is developed on account of an actual increase in the length of the style due to the cell-elongation or growth, as suggested by Merrell (12)

The florets appear to be all of the same type and those at the margin of the capitulum open first Generally, it takes from four to six days for all the florets of a capitulum to open The colour of the corolla becomes deeper with the fading of the flowers

The sequence of development of the floral parts agrees closely with the account presented by Martin (11) for *Aster*, Merrell (12) for *Silphium* and Bhargava (1) for *Eclipta* Merrell (12) found the calyx to be of the nature of



Text-figures 1–7. *Carthamus tinctorius* Development of the flower Figs 1 and 2. The flower primordia and the appearance of petals, Fig 3. The origin of stamens; Fig 4. The first appearance of calyx as angular projections, Fig 5 Development of the sepals and carpels; Figs. 6 and 7 The further development of the different floral whorls as also the origin of the ovule. × 100.

rudimentary pappus composed of two or three whorls of short hairs Each hair being composed of about three cells In *Carthamus* no differentiation of the calyx was noted

As noted in other species of the Compositæ, the nectary was found to occur in the form of a ring at the base of the style (Text-fig 7)

(*b*) *Microsporogenesis*—In the early stages of its development the anther is composed of a mass of homogenous cells which are polygonal in outline and are in an active state of division The origin of the archesporial cells in the anther could not be definitely traced It appears that they develop in the hypodermal layer, cut off a parietal layer, and then differentiate as the sporogenous cells In very young anthers the sporogenous cells have been observed to occur in the third layer, they could be easily made out on account of their larger size, denser cytoplasm, and chromaticity of the nucleus At first the sporogenous cells are only one layer thick, very soon, however, they divide by oblique walls and become two layered

Small (18) observed the occurrence of the archesporium to be distinctly hypodermal in *Senecio vulgaris* Merrell (12) also noted the presence of a single hypodermal cell in *Silphium*, which by division gave rise to the primary parietal and primary sporogenous cells Longitudinal division of the primary sporogenous cells finally gave rise to a mass of four or five cells in cross section Bhargava (1) working on *Eclipta erecta* states, 'the archesporial cells are rather late in differentiation and cannot be distinguished from the other cells of the anther till a parietal cell has been formed on the outside'

The microspore mother cells in the resting stage are mostly polygonal in outline and have dense cytoplasm and conspicuous nuclei The nuclear membrane is well defined and the nuclear cavity is filled up with a granular substance which is disposed mostly at the periphery (Plate I, fig 1) With the onset of prophase the nuclear cavity shows the presence of a number of coiled threads which on close examination show the presence of two chromonemata closely intertwined (Plate I, fig 2) Gregory (8) working on *Elettaria* has observed a similar appearance of the prophasic nucleus The reticulum gradually contracts away from the nuclear membrane (Plate I, fig 3) and the contracted knot (synizetic knot) generally lies on one side of the nuclear cavity enclosing the nucleolus in its meshes The synizetic knot is very tight and it is very difficult to follow the arrangement of the threads inside it Figure 4 (Plate I) represents a stage of synizesis In no case was a distinct connection of the nucleolus with the spireme noted, nor was there any evidence to suggest a transference of chromatic matter from the nucleolus to the spireme

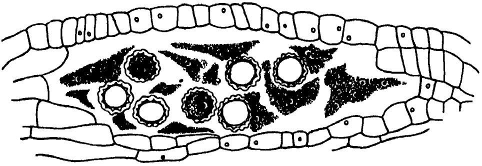
There are different views regarding the appearance of the synizetic knot which are too well known to be repeated The author concurs with the opinion of Gates and Nandi (4) expressed in a recent paper that, 'synizesis itself probably represents a sensitive condition of the nucleus when the delicate threads are easily compacted together by the entrance of the fixing agent'

There is distinct evidence as to the growth in size of the nucleus during synizesis and post-synizetic stages This confirms Gates and Rees' (5) observation on *Lactuca*

The contracted spireme gradually unravels itself and loops are thrown out from the contracted mass The spireme emerges as a more or less continuous thread (Plate I, fig 5) though occasionally free ends may be observed Parallelism of the threads is not apparent at this stage but at the next stage certain portions of the threads appear to be double in structure The thread gradually thickens as it fills up the nuclear cavity and appears as a loose coiled rope (Plate I, fig 6) This is the pachynema stage No distinct second contraction stage with radiating loops has been observed in this material, though the spireme was observed to be greatly convoluted before segmentation The segmented bits of spireme show their double nature very clearly (Plate I, fig 7) and from the nature of the segments, and the absence of the bronchonema stage, it appears that chromosome conjugation is of the parasynaptic type in this plant The segmented bits of spireme next thicken and shorten to form the typical bivalent chromosomes (Plate I, fig 8) At this stage the nuclear membrane becomes indistinct and the nucleolus also becomes reduced in volume though its chromaticity remains the same as before Gradually the bivalent chromosomes reach their maximum condensation and the nucleolus becomes smaller and paler in appearance and finally disappears At this stage the pollen mother cells separate from one another and round off In the different species of *Lactuca* studied by Gates and Rees (5) the pollen mother cells frequently separated from one another even before synapsis Such a condition is, however, rarely met with in plants

During diakinesis, the gemini which attain their maximum condensation generally lie scattered at the periphery of the nuclear cavity The two members of a bivalent pair generally lie side by side but some of them show the presence of chiasma During this stage the nuclear cavity shows the presence of faintly staining delicate fibres from which a multipolar spindle is organized The multipolar spindle very soon assumes the bipolar form and the chromosomes are arranged in a regular manner in the equatorial region of the spindle (Plate I, fig 9) Though the chromosomes are very much condensed yet their bivalent nature can be made out while they are oriented on the spindle A polar view of an equatorial plate at this stage clearly shows 12 bivalent chromosomes (Plate I, fig 13) The anaphasic separation of the chromosomes appears to be quite regular and no irregularity in the movement or distribution of the chromosomes has been noted On reaching the poles the chromosomes at first clump together but very soon they separate and assume a filamentous structure in which two closely intertwined threads may be seen A nuclear membrane is secreted and the whole thing assumes the form of a phragmoplast (Plate I, fig. 10) The spindle fibres at this stage are represented by striations in the cytoplasm. The interkinetic stage is of short duration. During the homotypic division the spindles are arranged either at right angles, or parallel to each other (Plate I, fig 11) Polar views of equatorial plates show the presence of 12 chromosomes The chromosomes are somewhat curved and to a certain extent they resemble the somatic chromosomes As stated before, Patel and Narayana (15) also found 12 haploid chromosomes in the plants they studied But Gregory working on Coimbatore types found the $2n$ number to be 20 From the evidence obtained in the present investigation the haploid number of chromosomes in *Carthamus tinctorius* appears to be 12 It is at this stage that the protoplast secretes a mucilaginous substance which completely encases it As in division I, no irregularity during division II was noted On the completion of the division four nuclei are organized in which a few chromatic dots and somewhat elongated chromosomes are noted The four nuclei are, however, seen to be connected to one another by fine striations of the cytoplasm which disappear later Cytokinesis takes place by the method of furrowing The furrows originate at the periphery equidistant from one another and gradually cut inwards and meet at the centre The young microspores at first lie enclosed in the mucilaginous envelope (Plate I, fig 12), but gradually this envelope disorganizes, and they lie free inside the microsporangium Each microspore when first liberated has a somewhat shrunken appearance (Plate I, fig 14) but they become round very soon, and the exine becomes slightly thickened and shows a number of fine spine-like projections They are uni-nucleate In optical sections the presence of three furrows is noted on the exine In surface view these appear as slits on the wall At this stage the tapetal tissue shows signs of activity As previously stated the tapetal cells are uni-nucleate, but they become bi-nucleate by mitotic division during the time when the pollen mother cells are in the synizetic stage Multinucleate tapetal cells have not been observed in this material The tapetal cells grow inwards, and send out projections in the anther cavity Very soon, however, the cytoplasms of the different cells fuse and a plasmodium is formed which fills the anther cavity and surrounds the young microspores The tapetal nuclei lie freely distributed in the plasmodium and some of them are seen to lie close to the young microspores (Text-fig 8) The nuclei are irregular in shape and contain fine chromatin granules Juel (10) and Tischler (20) working independently on *Silphium laciniatum* observed that the tapetal cells get in between the pollen grains, but they do not fuse completely The plasmodium, though it encloses the young microspores, is only in contact with the tips or spinous projections of the microspores in the initial stages But later, with the disorganization of the plasmodium, it is observed that a certain amount of the plasmodium substance has been incorporated on the exine which now becomes very thick and shows a number of blunt projections (Text-fig 9) It is interesting to note that Merrell (12) working on *Silphium* observed collection of plasma around the spores which were later encrusted by it in the form of a sheath The pollen grains though uni-nucleate at this stage show prophasic changes in the nuclei.

The mature pollen grains have three germpores Three nucleate pollen grains have been noted in *Carduus* and *Centaurea* in the tribe Cynareæ



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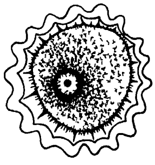

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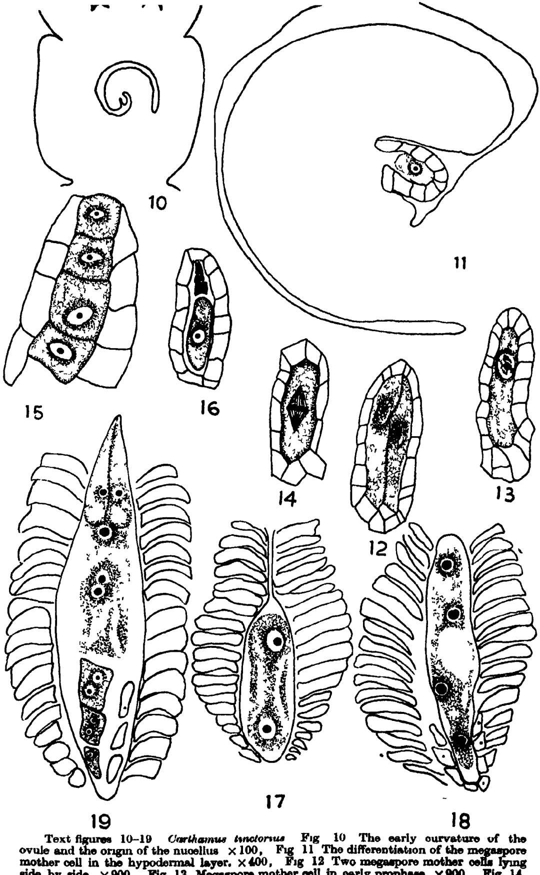
Text-figures 8 and 9. *Carthamus tinctorius* Fig 8 Pollen grains surrounded by tapetal plasmodium. × 300, Fig. 9 A pollen grain on the outer surface of which the plasmodial substance has been incorporated. × 1800

(c) *The Development of the megaspores and the embryo-sac* —When the microspore mother cells are in the synizetic stage a short blunt hemispherical protuberance is seen in the ovarian cavity Its position is slightly posterior and it grows obliquely upwards This is the ovule primordium, which very soon curves inwards and from the centre of this body a tiny protuberance—the nucellus—three cells in thickness, projects out (Text-fig 10) The integument next becomes differentiated It grows more rapidly than the nucellus and by its curvature brings about an anatropous condition of the ovule, even before the differentiation of the megaspore mother cell Very soon a hypodermal cell at the tip of the nucellus becomes differentiated as the archesporial cell and directly functions as the megaspore mother cell (Text-fig 11) Two megaspore mother cells lying side by side have been noted in some preparations (Text-fig 12) Schnarf (16) mentions the occurrence of two megaspore mother cells in *Adenostyles alliariæ* The nucellus at this stage is long and very much reduced and a single layer of epidermal cells enclose it completely. The integument at this stage becomes clearly differentiated as shown in text-figure 11 The megaspore mother cell next increases in size and then passes through the various stages of reduction division (Text-figs 13 and 14) On the completion of the homotypic division a linear tetrad of macrospores is produced (Text-fig 15) No 'T-shaped' tetrad has been observed The chalazal macrospore alone functions while the rest degenerate (Text-fig 16) It is interesting to note that in the tribe Calenduleæ the micropylar megaspore usually forms the embryo-sac, while in the tribes Astereæ, Cichorieæ and Senecioneæ either the micropylar or the chalazal megaspore has been found to function During the linear tetrad stage the epidermal cells covering the nucellus first show signs of degeneration The functional megaspore soon divides to form the two nucleate embryo-sac A central vacuole is noted and the nuclei become equally distributed at the two poles (Text-fig 17) At this stage the cells of the micropylar canal grow out in the form of hairs Other investigators have noted the presence of such hairs in a number of Compositæ These hairs are rich in plasma and are always directed towards the egg-apparatus The quadri-nucleate stage is next reached and the organization of the embryo-sac remains the same as before (Text-fig 18) At this stage the embryo-sac is considerably elongated and the epidermal cells surrounding the nucellus have degenerated completely, and the integumentary cells immediately surrounding the embryo-sac have become well differentiated and increased considerably in a radial direction These cells form what is commonly referred to as the 'integumentary jacket' (Text-fig 17) The eight nucleate stage, which follows soon, shows an increased size of the embryo-sac cavity as well as the vacuole in the centre The nuclei are distributed equally at the two poles of the embryo-sac The mature embryo-sac is typical of the angiosperms, but it is somewhat broader in the central region and constricted at the two ends Due to the disintegration of the nucellar cells capping the embryo-sac, the tips of the synergids project out and lie inside the micropylar cavity (Text-fig 19) The synergids have very pointed beaks and dense cytoplasm at the distal portion and the nucleus lies just above the vacuole which is placed at the proximal end The presence of synergid haustoria which has been found by Dahlgreen (2) and others in some plants of this family has, however, not been observed The egg is suspended between the synergids and has a large vacuole at its upper portion, and its nucleus is larger than that of the synergids The two polar nuclei lie very close together and in the centre of the embryo sac Prior to fertilisation they fuse, the fusion nucleus appears to be larger than the egg nucleus, and the nucleolus shows the presence of a large number of vacuoles This has also been noted by Merrell (12) Opperman (14) working on *Aster* states that in some instances fusion of the polar nuclei may be delayed until the time of fertilisation, but ordinarily the fusion takes place before the pollen tube discharges its contents into the embryo-sac The antipodal cells, which are three in number, are usually situated one above the other in a row, they lie in the chalazal end of the embryo-sac The nuclei of the antipodal cells soon divide and very soon two nuclei are seen in most of the antipodal cells A similar condition of the



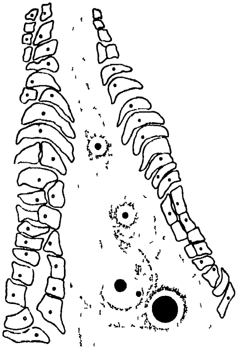
Text figures 10–19 *Carthamus tinctorius* Fig 10 The early curvature of the ovule and the origin of the nucellus ×100, Fig 11 The differentiation of the megaspore mother cell in the hypodermal layer. ×400, Fig 12 Two megaspore mother cells lying side by side. ×900, Fig 13 Megaspore mother cell in early prophase ×900, Fig 14 Heterotypic division. ×900, Fig. 15 Linear tetrad of megaspores. ×1600; Fig. 16 Functional megaspore and three degenerated megaspores. ×900; Fig. 17. Binucleate stage of the embryo-sac. ×900, Fig. 18 Quadrinucleate stage of the embryo-sac. ×900;

antipodal cells has been recorded in *Dahlia variabilis* and *Tagetes signatus.* Schnarf (16) gives a complete account of the variation in the number and form of the antipodal cells in different tribes of the Compositæ He, however, states that no information is available as to the nature of the antipodals in Cynareæ Tackholm (19) has reported as many as forty nuclei in an antipodal cell of *Cosmidium burridgeanum* and Merrell (12) also gives an account of the variations that are commonly noted in antipodal cells

(*d*) *Fertilisation* —The ovule, as also the embryo-sac, elongate considerably before the entry of the pollen tube, and the egg also becomes very much elongated The nucleus lies at the lower portion and a big vacuole lies above it The secondary nucleus lies close to the egg At the time of the entry of the pollen tube no trace of the synergids or antipodals are noted in the embryo-sac Synergids were, however, noted to be present at the time of fertilisation by Mottier (13) in *Senecio* The pollen tube enters the embryo-sac through the micropyle Porogamy appears to be the rule in this family, but Doll (3) found two cases of chalazogamy in *Blainvillea rhomboidea* The tip of the pollen tube appears to be somewhat swollen when inside the embryo-sac cavity (Text-fig 20) It appears that the vegetative nucleus degenerates before the pollen tube enters the micropyle, as it was not observed in any preparation On the other hand a number of preparations showed the presence of two small nuclei, one preceding the other and lying very close to the tip of the pollen tube Such nuclei were also seen in the embryo-sac cavity close to the egg and the secondary nucleus From these facts, one is inclined to believe that these are the generative nuclei Actual fusion of the male and the female gametes, or the process of double fertilisation has not been observed

The form of the generative nuclei in *Carthamus* appears to be spherical Spherical generative nuclei have also been observed by Mottier (13) and others working on the family Compositæ Merrell (12) states that the male nuclei when first formed are approximately spherical, but in the later stages they become very much elongated and resolve into a spiral He further states that preparations showing the nuclei at the tip of the pollen tube indicate that the sex nuclei have assumed a spherical form

(*e*) *Endosperm and Embryo* —After fertilisation the egg rests for some time before it commences activity The definitive nucleus, however, divides very soon Though the first division of the definitive nucleus has not been observed, yet the presence of a few nuclei at the micropylar end of the embryo-sac and close to the fertilised egg undoubtedly indicates that it divides first The endosperm is of the nuclear type, and grows by mitotic division No irregularity in the different stages of division has been observed Although it has not been possible to count accurately the number of chromosomes in the endosperm nuclei, yet it can safely be stated that it is more than the 2*n* number of the plant With the increase in size of the embryo-sac cavity the endosperm cells divide rapidly and form a lining layer around the sac It later fills in the embryo-sac cavity from the chalazal and micropylar ends At this stage wall formation of the endosperm cells is noted first at the micropylar end



Text-fig 20 *Carthamus tinctorius* Pollen tube with the generative nuclei. ×800

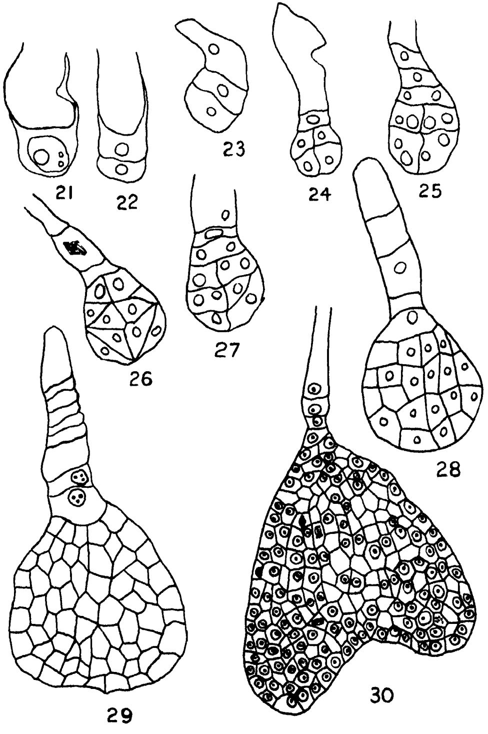
and gradually extends downwards The nuclei of the endosperm cells contain many nucleoli which, however, differ in size It is interesting to note that the egg after syngamy increases in size and becomes considerably elongated It appears as if it was suspended by two cytoplasmic strands from the micropylar end of the embryo-sac (Text-fig 21) The first division is transverse, resulting in an apical and a basal cell, of which the former is considerably larger than the latter (Text-fig 22) As observed in many other species of the Compositæ, the basal cell forms the greater part of the embryo, and the apical cell by division forms the suspensor and part of the embryo The apical cell later divides by a transverse wall and a three-celled pro-embryo is produced (Text-fig 23) The terminal cell of the pro-embryo next divides by an anticlinical wall, followed very soon by periclinical walls to form the quadrant stage of the embryo (Text-fig 24) At this stage the embryo becomes globular in outline

In the octant stage the four superior octants give rise to the cotyledons and the stem tip, while the four inferior octants give rise to the hypocotyl and the primary root The hypophysis cell, which becomes differentiated at an early stage of the development of the embryo, generally divides when the three histogenic layers are laid down, and contributes to the apex of the root

The first division of the hypophysis cell in this plant is longitudinal as shown in Text-figs 25, 26 and 27 Its later divisions have not been traced

Text-fig 30 shows the development of the cotyledons The differentiation of the stem tip has not been observed and it appears to differentiate very late

The suspensor generally consists of four cells but in certain cases it was found to consist of 8 cells (Text-figs 28 and 29).



Text figures 21–30. *Carthamus tinctorius.* **Stages in the development of the mbryo. × 500**

Text-fig 30 shows the cotyledon with the three histogenic layers differentiated

SUMMARY

The paper gives an account of the development of the flower, pollen grains, and the embryology of *Carthamus tinctorius*

1 The development of the floral parts occurs in the following succession —petals, stamens, sepals and carpels The sepals do not become differentiated but remain as minute angular projections The opening of the florets takes place from the periphery inwards, and it takes from four to six days for all the florets of the capitulum to open

2 In the early stages of the development of the microspore mother cells the nucleus shows the presence of a number of coiled threads which appear to be double The threads contract into a tight knot and on recovery from synizesis the double nature of the spireme is not seen Chromosome conjugation is of the parasynaptic type There are twelve diplotene pairs which show the presence of terminal and interstitial chiasma The haploid number of chromosomes is 12 The chromonematic structure of the chromosomes is apparent at the interkinetic stage After the II division the microspores are enveloped in a mucilaginous pellicle and show a tetrahedral arrangement

3 The tapetal cells of the anther develop into a plasmodium which fills the anther loculus completely when the young microspores are formed Some of the plasmodial substance appear to be incorporated on the spiny exine of the pollen grains which then becomes differentiated as blunt processes The microspores have three germ pores

4. The development of the female gametophyte is of the normal type The megaspore mother cell is hypodermal in origin Two megaspore mother cells have been noted to occur side by side A linear tetrad of megaspores is produced The chalazal megaspore becomes functional and gives rise to an eight nucleate embryo-sac The mature embryo-sac is of the normal angiospermous type The antipodals are binucleate The cells of the integument lining the micropyle grow out in the form of hairs and these are directed towards the egg apparatus

5 Fertilisation is porogamous The synergids and the antipodals degenerate completely before the entrance of the pollen tube into the embryo-sac The secondary nucleus lies very close to the egg at the time of fertilisation The sperms appear as spherical nuclei

6 The division of the endosperm nucleus occurs prior to that of the egg and the endosperm is of the nuclear type The zygote divides first by a transverse wall The further development of the embryo appears to be that of a *Capsella* type The suspensor is composed of four to eight cells The three histogenic layers become differentiated in the embryo before it attains full development

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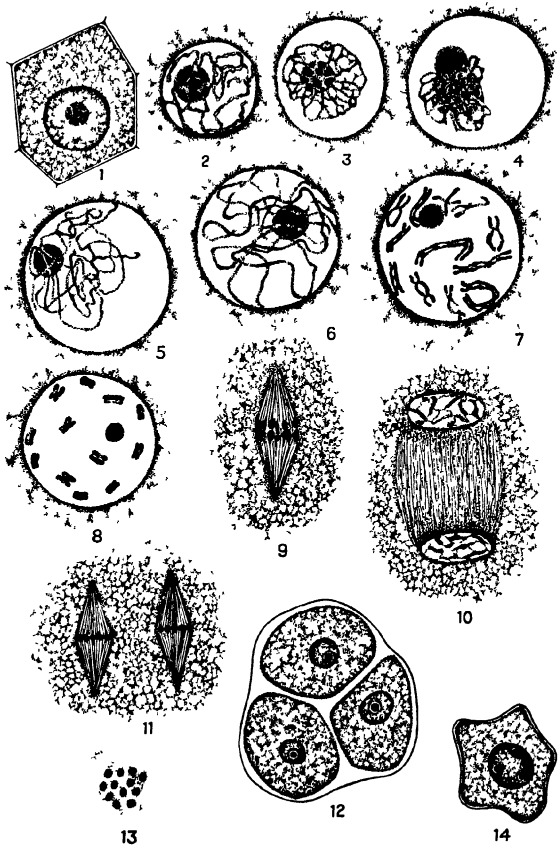
Explanation of Plate I

Carthamus tinctorius Linn

Fig 1 A sporogenous cell showing the formation of reticulum
Fig 2 Early prophase The chromonematic structure of the chromosomes seen
Figs 3 and 4 Stages in synizesis
Fig 5 Recovery of the nucleus from synapsis
Fig 6 Pachynema
Fig 7 Early diakinesis The presence of chiasma evident in the bi valents
Fig 8 Diakinesis
Fig 9 Heterotypic metaphase
Fig 10 Interkinesis The chromosomes connected by anastomoses
Fig 11 Homotypic division
Fig 12. Pollen tetrad enclosed by a mucilaginous membrane Tetrahedral arrangement
Fig 13 Polar view of an equatorial plate (1st Div), 12 chromosomes seen
Fig 14 A microspore not fully developed

All figures were drawn with the aid of a camera lucida at a magnification. × 1600.



Carthamus tinctorius Linn

ON THE PHOTO-IONIZATION OF MOLECULES.

By B. D Nag-Chowdhuri, *M Sc*, *late Research Scholar, Allahabad University*
and K Basu, *D Sc*, *Calcutta University*

(Communicated by Prof M N Saha, D Sc, F R S)

(*Read January 2, 1940*)

1. Introduction

The subject of photo-ionization of molecules has hitherto received scant attention both from experimenters and theoretical physicists The importance of the subject was first pointed out by Prof M N Saha (1935), who suggested that the electrons in the ionosphere may, in part, be due to the ionization of N_2 to N_2^+ and O_2 to O_2^+, each in two different ways The present attempt dealing theoretically with the photo-ionization of H_2 to H_2^+ was made at the suggestion of Prof Saha, as it was felt that the cases of N_2 and O_2 are rather too complex and a start might be made with the H_2-molecule in this direction, on account of simplicity of structure of the latter

We have not been able to trace any previous theoretical attempt on this problem Regarding the experimental work, the following report in *Die Physik* by Joos and Finkelnburg (1935) and Prof Saha's remarks on the same may prove interesting·

'Ionization continua of molecules have not been demonstrated so far, and the only attempt hitherto known to explain absorption continua of a polyatomic molecule was by Henning (*Ann der Physik*, 13, 599, 1544) and the ionization spectrum is not at all convincing. Since the ionization continua must naturally be possible also in the case of molecules, it remains to be investigated why photo-ionization of molecules is apparently such an improbable process The scheme of molecular potential curves of which we shall speak later (Section on molecular continuum), and the Frank-Condon Principle which controls transitions between molecular states appear to offer a possibility for its explanation. In the term-scheme, it is usually found that the continuous eigen-spectrum corresponding to ionization are usually superposed on the continuous eigen-value region of different excited states which lead to dissociation. According to Frank-Condon Principle, the transitions from the ground state are very probable, and if we consider the part of the transition-probability due to the electron it is apparently more probable than transitions to the continuous eigen-value spectrum corresponding to ionisation. The following observations seem to hold generally:—

The ionisation of a molecule by light-quanta appear to be less probable than dissociation of the molecule by absorption of the same light-quanta into

VOL. VI—No. 1. [Published April 30th, 1940.

a normal and an excited atom with a certain amount of kinetic energy In this way, we can understand why extended intensive dissociation continua of molecules have been obtained, while molecular photo-ionization has not been shown '

With respect to the above remarks Dr Saha has been kind enough to communicate to us the following —

'While agreeing mostly with those remarks, it may be pointed out that Joos and Finkelnburg have probably omitted to mention one significant cause of the absence of any experimental proof of molecular photo-ionization In the case of most of the ordinary gases, this lies in a region where absorption experiments are extremely difficult, and have not therefore been properly carried out For example, for H_2 it begins at λ 840, for O_2 at λ 1019 (feeble) and at λ 747 (strong), for N_2 at λ 794 (feeble) and at λ 660 (strong) The same remark may be made with respect to other gases The other cause mentioned by Joos and Finkelnburg is of course effective, but the proportion of photons which cause dissociation may be widely different for different gases and needs investigation '

Let us see how previous workers are correct in their assumptions on the variation of photo-ionization with frequency Let us denote the absorption coefficient by $\tau(\nu)$ and the frequency by ν Pannekoek (1926) and Chapman (1931) assumed that the $\tau(\nu)/\nu$-curve for molecular photo-ionization is of the same nature as the atomic photo-ionization curve, *i e* $\tau(\nu)$ begins with a maximum value at the threshold value of $\nu = \nu_0$, $h\nu_0 = eV_1$ where V_1 = the ionization potential, but diminishes with increasing ν as $1/\nu^3$ roughly It is evident that this assumption is incorrect for molecular photo-ionization, for, the case of molecules is complicated by the fact that the nuclear distance changes in course of ionization We illustrate by taking the case of the H_2-molecule The process of ionization of H_2 may be illustrated symbolically as

$$1s\sigma\ 1s\sigma \rightarrow 1s\sigma\ np\ (\sigma p)$$
$$\text{or } 1s\sigma\ 1s\sigma \rightarrow 1s\sigma\ ns\sigma$$

i e one electron goes to infinity by having its *l*-quantum changing from 0(1*s*) to 1(*mp*) and the total quantum number $n \rightarrow \infty$ But the nuclear distance in normal H_2 is 0 749×10^{-8} cms while in normal H_2^+ it is 1·070×10^{-8} cms. According to the Frank-Condon Principle, during an electron-transition, the nuclear distance remains unchanged, when applied to the present case, this means that H_2^+ -ion will be left in a vibrational state, with a large value of V, the vibrational quantum number Hence the strongest transition will be from $V'' = 0$ to V' = some integral number, but the transition $V'' = 0$ to $V' = 0$ is expected to be rather feeble, as the nuclear distance in H_2^+ for $V' = 0$, *viz.*, the 1·070×10^{-8} cm is very different from the nuclear distance in H_2, *viz*, 0·709×10^{-8} cm Hence, the lowest frequency $\nu = \nu_0 + \frac{1}{2}\omega_0'$ (ν_0 being the electronic transition frequency, ω_0' = normal frequency of nuclear vibration of

H_2^+) will be rather very feebly absorbed The strongest absorption will take place at the frequency $\nu = \nu_0 + (V' + \frac{1}{2})\,\omega_0'$ where V' is the particular quantum number for that vibration of H_2^+ when the least distance between the nuclei of H_2^+ is $0{\cdot}709 \times 10^{-8}$ cm

The investigations which are reported below have confirmed these expectations

2. Calculation of Photo-ionization

Let $I_{0\nu}$ be the intensity of a beam of light of frequency ν initially, and $I_{l\nu}$ the intensity after the beam has passed through a length l cms of a gas at N.T P Then we have

$$I_{l\nu} = I_{0\nu} \exp(-\alpha_\nu l) = I_{0\nu} \exp(\tau(\nu)Nl) \quad . \quad (1)$$

where $\tau(\nu)$ is absorption per molecule, N the number of molecules per c c. Then the absorption coefficient $\tau(\nu)$ as given by Bethe (1933) is given by

$$\tau(\nu)\,d\nu = \frac{8\pi^3\nu}{hc} \left| M_{kk'} \right|^2 dE \quad . \quad . \quad .. \quad (2)$$

where $|M_{kk'}|$ denotes the transition probability from a state k to k' associated with the absorption of a photon $h\nu$, and dE, the range in energy In the present case, we should remember that the transition is from a 'bound' state of the electron in the hydrogen molecule to a 'free' state of the electron in the ionized hydrogen molecule The matrix component in Eq (2) is defined by the equation

$$|M_{kk'}| = \int \psi_k [M] \psi_{k'}\, d\Omega \quad .. \quad .. \quad .. \quad .. \quad (3)$$

where ψ_k is the wave function of the initial state (of the H_2 molecule), $\psi_{k'}$ that of the final state (of the molecule with the 'free' electron in a continuous energy state), [M] is the electric moment (a function of all the co-ordinates involved), and the integration extends throughout the entire space whose element is $d\Omega$

The assumption we have to make in our case is, as proposed by Born and Oppenheimer (1927) and followed by Hutchisson (1930), that the eigen-functions $\psi_k(H_2)$, $\psi_{k'}(H_2^+ : e)$ are products of electronic, vibrational and rotational eigen-functions, further, let us assume that the functions $\psi_k(H_2)$ and $\psi_{k'}(H_2^+ : e)$ are normalized, and the nuclear distance is regarded as a constant parameter while the integration is carried out over the electronic co-ordinates.

We proceed according to Condon (1928) and Hutchisson (1930), and split up the electric moment [M] into sum of two moments, *i.e.* $[M] = M_e(r) + M_v(q)$ where $M_e(r)$ is the electric moment associated with the electronic transition and $M_v(q)$ that associated with the vibrational transition corresponding to a change in the internuclear distance q. Next, let us split up the eigen-functions $\psi(H_2)$ and $\psi(H_2^+ : e)$ into $\psi_1(e)\psi_1(v)\psi_1(m)$ and $\psi_2(e)\psi_2(v)\psi_2(m)$, where e, v, m respectively stand for electronic, vibrational and rotational motions The suffixes 1 and 2 in the eigen-functions refer respectively to the initial (H_2) and final ($H_2^+ \ e$) states Thus $\psi_1(m)$ denotes the eigen-function for rotation only in the initial state, and $\psi_2(m)$ the same in the final state Similar interpretations are implied for the functions $\psi_1(v)$, $\psi_2(v)$ and $\psi_1(e)$, $\psi_2(e)$ One must guard against the confusion that $\psi_1(m)$, $\psi_1(v)$, $\psi_1(e)$ are the same functions of m, v, e anymore than $\psi_2(m)$, $\psi_2(v)$, $\psi_2(e)$ are the same functions of m, v, e respectively To avoid cumbersome notations with regard to the above functions, we have used these simplifications, whose import is quite evident

Splitting up the eigen-functions of $\psi(H_2)$ and $\psi(H_2^+ \ e)$ into $\psi_1(e)\psi_1(v)\psi_1(m)$ and $\psi_2(e)\psi_2(v)\psi_2(m)$ respectively, we get

$$
\begin{aligned}
|M_{kk'}| &= \iiint \psi_1(e)\psi_1(v)\psi_1(m)[M]\psi_2(e)\psi_2(v)\psi_2(m)d\Omega \\
&= \int \psi_1(m)\psi_2(m)d\phi \iint \psi_1(e)\psi_1(v)[M_e(r)+M_v(q)]\psi_2(e)\psi_2(v)d\Omega_e d\Omega_v \qquad (4)
\end{aligned}
$$

where $\int \ d\Omega_e, \int \ .d\Omega_v$ denote integration with respect to electron co-ordinates and nuclear co-ordinates respectively The above can be further split up into principal parts Thus

$$
\begin{aligned}
|M_{kk'}| = \int \psi_1(m)\psi_2(m)d\phi \Big[&\int \psi_1(e)\psi_2(e)d\Omega_e \int \psi_1(v)M_v(q)\psi_2(v)d\Omega_v \\
&+ \int \psi_1(v)\psi_2(v)d\Omega_v \int \psi_1(e)M_e(r)\psi_2(e)d\Omega_e \Big] \qquad (5)
\end{aligned}
$$

The H_2^+ -ion together with the electron in the continuous energy state can be regarded as an excited state of the normal H_2-molecule This means that $\psi_1(e)$ and $\psi_2(e)$ are orthogonal to each other, and consequently the contribution of the first part to $|M_{kk'}|$ is nil The contribution due to the second part cannot be zero, in general, as the vibrational states do not refer to the same molecule, i e $\int \psi_1(v)\psi_2(v)d\Omega_v \neq 0$ The transition probability thus reduces to

$$|M_{kk'}| = \int \psi_1(m)\psi_2(m)d\phi \int \psi_1(v)\psi_2(v)d\Omega_v \int \psi_1(e)M_e(r)\psi_2(e)d\Omega_e \qquad (6)$$

The first factor of $|M_{kk'}|$ *viz*, $\int \psi_1(m)\psi_2(m)d\phi$ involves the rotational states, and, at any rate, contributes a constant which may be taken to be unity, whatever be the nature of transitions (vide Condon, *Phys Rev*, Vol 32, p 858, 1928, line 9), we may leave this part out of account for our future treatment. The second factor, *viz*, $\int \psi_1(v)\psi_2(v)d\Omega_v$ concerns nuclear oscillation This is taken up subsequently. We consider now the third factor, *viz*, $\int \psi_1(e)M_e(r)\psi_2(e)d\Omega_e$ Here $\psi_1(e)$ denotes the lowest state of the H_2-molecule which can be regarded as being made up of two H-atoms in the 1*s* states. We have therefore

$$\psi_1(e) = \frac{1}{\sqrt{2 \pm S}} \Big[u(a1)_{1s} \, u(b2)_{1s} \pm u(a2)_{1s} \, u(b1)_{1s} \Big] \qquad .. \quad (7)$$

where $u(a1)_{1s}$ is the normalized wave-function of the H-atom with electron (1) in the 1*s*-state with respect to nucleus (a). Similarly for the other u's.

In Hartree units we have (vide Bethe, *Handbuch der Physik*, 24, p 284, Eq (3. 18), 1934):

$$\left.\begin{aligned} u(a1)_{1s} &= 2\exp(-r_{a1})\,, & u(a2)_{1s} &= 2\exp(-r_{a2})\,, \\ u(b1)_{1s} &= 2\exp(-r_{b1})\,, & u(b2)_{1s} &= 2\exp(-r_{b2})\,, \end{aligned}\right\} \tag{8}$$

and

$$\begin{aligned} S^2 &= \iint u(a1)_{1s}\, u(b1)_{1s}\, u(a2)_{1s}\, u(b2)_{1s}\, d\Omega_1\, d\Omega_2 \\ &= \left[\int u(a1)_{1s}\, u(b1)_{1s}\right]^2. \end{aligned} \tag{9}$$

The integral S was originally introduced by Sugiura (1927) and has the value $(1+q+q^2/3)\exp(-q)$ in Hartree units, q = nuclear distance in the same units As is well known $\psi_1(e)$, as expressed by (7), is only an approximate form and represents the zeroeth order of approximation

As regards $\psi_2(e)$, the wave function of H_2^+ and the free electron, we can follow the method of Heitler and London (1927), by replacing one of the eigenfunctions by a continuous eigen-function denoting ∞S-state Further improvements on the Heitler-London model of H_2 have been worked out by Wang (1928), Hylleraas (1931) and others, but for the present we stick to the HL-model

Let $u(a1)_{cs}$ represent the normalized wave function for the continuous state of the H-atom, the electron 1 being in a continuous positive energy state with respect to the nucleus '*a*' and let '*cs*' denote that the electron is in the continuous energy state with $l = 0$ The energy of the free electron may be anything from 0 to ∞ Similarly, the continuous state may be a *p*- or a *d*-state represented by $u(a1)_{cp}$ or $u(a1)_{cd}$ and so on Following Kemble and Zener (1929), we may consider the wave-functions of the excited states of H_2^+-molecule as built up of an excited H-atom and a normal H-atom, the electron in the excited H-atom being in the ∞*s* or ∞*p* states The ∞*p* state again gives 3 ψ-functions according as the *m*-quantum number is 1, 0, or -1 Thus there will be four ψ-functions representing the H_2^+-molecule which consist of the first electron in the 1*s*-state with respect to the nucleus '*a*', and the second electron in ∞*s* or ∞*p* $(1, 0, -1)$ state with regard to nucleus '*b*' If we exchange nuclei, or electrons, or both, we get three more sets of wave-functions Each set consists of 4 wave-functions denoting the ∞*s* and ∞*p* $(1, 0, -1)$ states. These are Kemble and Zener's 16 wave-functions Exactly similar expressions may be obtained for the electrons in the continuous state, which may be ∞*d* or ∞*f* states, etc , giving an infinite number of wave-functions

At the outset, however, we shall confine our attention, for the sake of simplicity of treatment, to the simplest transition, *viz* , from $1s^2$ to (1*s*∞*s*) state This gives us only the $^1\Sigma_u$-state, but other $^1\Sigma$-states with the same energy-value will arise, from combination 1*s*∞*p*σ, 1*s*∞*d*σ, but these are not considered here. We obtain, in that case, four wave-functions by interchange of nuclear and electronic co-ordinates. These are

$$\left.\begin{aligned}\psi(1) &= u(a1)_{1s}\,u(b2)_{cs}\,; \quad \psi(2) = u(a2)_{1s}\,u(b1)_{cs}\,,\\ \psi(3) &= u(a2)_{cs}\,u(b1)_{1s}\,; \quad \psi(4) = u(a1)_{cs}\,u(b2)_{1s}\,;\end{aligned}\right\} \quad . \tag{10}$$

where

$$u(a1)_{cs} = -\frac{\sqrt{2}}{\sqrt{1-\exp(-2\pi n')}}\cdot\frac{1}{2kr_{a1}}\times$$

$$\frac{1}{2\pi}\oint_{\xi}(\xi+\tfrac{1}{2})^{-in'-1}\,(\xi-\tfrac{1}{2})^{in'-1}\exp(-2ikr_{a1}\xi)d\xi \quad . \tag{11}$$

and the contour is taken along a path enclosing the two branch-points at $\xi = \pm\frac{1}{2}$ For the above expression see Bethe, *loc cit*, p 293, formula (4 22) In this latter formula put $l = 0$ and we get to the result (11) This method of writing out the eigen-function of (H_2^+, and e) is of course approximate, as in the original treatment of H_2 by Heitler and London, but further improvements may be taken up later on

We observe that $\psi(3)$ is obtained from $\psi(1)$, by interchange of 'a' and 'b', $\psi(4)$ from $\psi(2)$, by interchange of 'a' and 'b', $\psi(2)$ from $\psi(1)$, by interchange of 1 and 2, $\psi(4)$ from $\psi(3)$, by interchange of 1 and 2

Using the symbols S^E, A^E, S^N, A^N to denote symmetry in the wave-functions for an interchange of electronic and nuclear co-ordinates, or anti-symmetry for the same, we form the wave-functions of the H-ion, as a linear combination of $\psi(1)$, $\psi(2)$, $\psi(3)$, $\psi(4)$ and indicate its symmetry or anti-symmetry in the electrons or nuclei Thus

$$\psi(H_2^+ : e)\quad \left.\begin{aligned}\phi_1 &= C_1[\psi(1)+\psi(2)+\psi(3)+\psi(4)]\,,\ (S^ES^N)\\ \phi_2 &= C_2[\psi(1)+\psi(2)-\psi(3)-\psi(4)]\,,\ (S^EA^N)\\ \phi_3 &= C_3[\psi(1)-\psi(2)+\psi(3)-\psi(4)]\,;\ (A^ES^N)\\ \phi_4 &= C_4[\psi(1)-\psi(2)-\psi(3)+\psi(4)]\,,\ (A^EA^N)\end{aligned}\right\} \quad .. \tag{12}$$

For normalization we notice that we should have

$$\int\phi_1^2d\Omega = \int\phi_2^2d\Omega = \int\phi_3^2d\Omega = \int\phi_4^2d\Omega = 1 \quad .. \tag{13}$$

Let us define the following integrals.

$$\left.\begin{aligned}A &= \int\psi(1)\psi(2)d\Omega = \int u(a1)_{1s}u(b1)_{cs}d\Omega_1\int u(a2)_{1s}u(b2)_{cs}d\Omega_2 = X^2;\\ B &= \int\psi(1)\psi(3)d\Omega = \int u(a1)_{1s}u(b1)_{1s}d\Omega_1\int u(a2)_{cs}u(b2)_{cs}d\Omega_2 = SY;\\ C &= \int\psi(1)\psi(4)d\Omega = \int u(a1)_{1s}u(a1)_{cs}d\Omega_1\int u(b2)_{1s}u(b2)_{cs}d\Omega_2 = O\,;\\ D &= \int\psi(2)\psi(3)d\Omega = \int u(b1)_{1s}u(b1)_{cs}d\Omega_1\int u(a2)_{1s}u(a2)_{cs}d\Omega_2 = O\,;\\ E &= \int\psi(2)\psi(4)d\Omega = \int u(a1)_{cs}u(b1)_{cs}d\Omega_1\int u(a2)_{1s}u(b2)_{1s}d\Omega_2 = SY;\\ F &= \int\psi(3)\psi(4)d\Omega = \int u(b1)_{1s}u(a1)_{cs}d\Omega_1\int u(b2)_{1s}u(a2)_{cs}d\Omega_2 = X^2.\end{aligned}\right\} \tag{14}$$

We notice that F is obtained from A by interchange of nuclei, E from B by interchange of electrons, and C from D by interchange of both nuclei and electrons Further, we have $A = F = X^2$ where X is the integral $\int u(a1)_{1s}u(b1)_{cs}d\Omega_1$. Similarly, we have $B = E = SY$ where $S = \int u(a1)_{1s}u(b1)_{1s}d\Omega_1$ and is the 'Suguira Integral', already referred to The integral $Y = \int u(a2)_{cs}u(b2)_{cs}d\Omega_2$ is entirely of a new type We observe, further, that integrals C and D are each equal to zero, from conditions of orthogonality We therefore have

$$\left.\begin{aligned}\iint\psi(1)\psi(2)d\Omega_1d\Omega_2 &= \iint\psi(3)\psi(4)d\Omega_1d\Omega_2 = X^2,\\ \iint\psi(1)\psi(3)d\Omega_1d\Omega_2 &= \iint\psi(2)\psi(4)d\Omega_1d\Omega_2 = SY.\end{aligned}\right\} \qquad (15)$$

Now the conditions deduced give us for the normalizing factors

$$\left.\begin{aligned}C_1 &= \frac{1}{2\sqrt{1+X^2+SY}}, & C_2 &= \frac{1}{2\sqrt{1+X^2-SY}},\\ C_3 &= \frac{1}{2\sqrt{1-X^2+SY}}, & C_4 &= \frac{1}{2\sqrt{1-S^2-SY}}\end{aligned}\right\} \qquad (16)$$

3 CALCULATION OF ELECTRONIC TRANSITION PROBABILITY

We have already stated that the nuclear distance is to be regarded as constant during electronic transition, but due to the vibrational transitions which accompany the electronic transitions this distance may change considerably The electric moment corresponding to electronic transition is given by

$$e\left(\vec{r}_{a1}+\vec{r}_{b1}+\vec{r}_{a2}+\vec{r}_{b2}\right) \qquad (17)$$

where $\vec{r}_{a1}$ etc denote vectors and the summation is vectorial Choosing the component of the electric moment along the internuclear axis, *i.e.*, our z-axis, we have

$$M_e(z) = e(r_{a1}\cos\theta_1+r_{b1}\cos\phi_1+r_{a2}\cos\theta_2+r_{b2}\cos\phi_2) \qquad (18)$$

where θ_1, θ_2, ϕ_1, ϕ_2 are the angles shown in Fig 1 We need not calculate

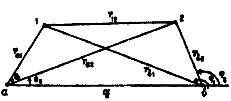


FIG 1.

the M $(x+iy)$ terms since they vanish due to the ϕ-part of the integral. The component perpendicular to the nuclear axis $= e(\rho_1e^{i\phi_1}+\rho_2e^{i\phi_2})$, where ρ_1, ρ_2 are the distances of electrons 1 and 2 from the internuclear axis, and ϕ_1, ϕ_2

the angles between the planes (1 *a b*), (2 *a b*) and a fixed plane in space passing through the internuclear axis

$$\therefore\ \mathrm{M}_e(x+iy)=\frac{\mathrm{CC}'}{q}\int\Big[(\psi_1'+\psi_2')\,[\rho_1e^{i\phi_1}+\rho_2e^{i\phi_2}]\big(\psi(1)+\psi(2)+\psi(3)+\psi(4)\big)\Big]d\Omega$$

for the transition $\psi(\mathrm{H}_2)$ $(\mathrm{S}^{\mathrm{F}}\ \mathrm{S}^{\mathrm{N}})\rightarrow\psi(\mathrm{H}_2{}^+\ e)$ $(\mathrm{S}^{\mathrm{E}}\ \mathrm{S}^{\mathrm{N}})$ [Cf Eqns 21–24 below]

Since ρ_1, ρ_2 are expressible in terms of q, r_{a1}, r_{b1}, etc from elementary trigonometry and the ψ's are functions of r_{a1}, r_{b1}, etc only, the above can be split up into sum of two integrals $\mathrm{M}_e{}^1(x+iy)$ and $\mathrm{M}_e{}^2$ $(x+iy)$ containing $e^{i\phi_1}d\phi_1$, $e^{i\phi_2}d\phi_2$ as factors respectively in the integrands Since the limits of those ϕ's are 0 and 2π for either of the electron-spaces, both $\mathrm{M}_e{}^1$ and $\mathrm{M}_e{}^2$ vanish on account of this zero factor Now we have

$$\left.\begin{aligned} r_{a1}\cos\theta_1+r_{b1}\cos\phi_1&=(r_{a1}{}^2-r_{b1}{}^2)/q=z_1\\ r_{a2}\cos\theta_2+r_{b2}\cos\phi_2&=(r_{a2}{}^2-r_{b2}{}^2)/q=z_2\end{aligned}\right\}\qquad(19)$$

So we derive

$$\mathrm{M}_e(z)=\mathrm{M}_e(z_1)+\mathrm{M}_e(z_2)\qquad(20)$$

where

$$\left.\begin{aligned}\mathrm{M}_e(z_1)&=\frac{e}{q}\,(r_{a1}{}^2-r_{b1}{}^2)\\ \mathrm{M}_e(z_2)&=\frac{e}{q}\,(r_{a2}{}^2-r_{b2}{}^2)\end{aligned}\right\}$$

We have further

$$\psi(\mathrm{H}_2)=\mathrm{C}(\psi_1'+\psi_2')\text{ or }\mathrm{C}'(\psi_1'-\psi_2')\qquad\ldots\quad(21)$$

where

$$\left.\begin{aligned}\psi_1'&=u(a1)_{1s}u(b2)_{1s}\\ \psi_2'&=u(a2)_{1s}u(b1)_{1s}\end{aligned}\right\}\qquad\ldots\quad(22)$$

and

$$\mathrm{C}=\frac{1}{\sqrt{2+2\mathrm{S}^2}},\quad \mathrm{C}'=\frac{1}{\sqrt{2-2\mathrm{S}^2}}.\qquad\ldots\quad\ldots\quad(23)$$

We now try to find out the $\mathrm{M}_e(z)$-value for the transition·

$$\psi(\mathrm{H}_2)(\mathrm{S}^{\mathrm{E}}\mathrm{S}^{\mathrm{N}})\rightarrow\psi(\mathrm{H}_2{}^+\,.\,e)(\mathrm{S}^{\mathrm{E}}\mathrm{S}^{\mathrm{N}})$$

We have

$$\mathrm{M}_e(z)=\frac{\mathrm{CC}'}{q}\int\Big[(\psi_1'+\psi_2')\{(r_{a1}{}^2-r_{b1}{}^2)+(r_{a2}{}^2-r_{b2}{}^2)\}\times$$
$$\times\{\psi(1)+\psi(2)+\psi(3)+\psi(4)\}\Big]d\Omega\ .\qquad(24)$$

In order to evaluate this integral, we have to deal with 32 terms. Let us first consider the product of the ψ's which are eight in number. These are

$$\left.\begin{aligned}
A' &= \psi_1'\psi(1) = u(a1)_{1s}u(a1)_{1s}u(b2)_{1s}u(b2)_{cs}\,;\\
B' &= \psi_1'\psi(2) = u(a1)_{1s}u(b1)_{cs}u(a2)_{1s}u(b2)_{1s}\,,\\
C' &= \psi_1'\psi(3) = u(a1)_{1s}u(b1)_{1s}u(b2)_{1s}u(a2)_{cs}\,;\\
D' &= \psi_1'\psi(4) = u(a1)_{1s}u(a1)_{cs}u(a2)_{1s}u(b2)_{1s}\,,\\
E' &= \psi_2'\psi(1) = u(a1)_{1s}u(b1)_{1s}u(a2)_{1s}u(b2)_{cs}\,,\\
F' &= \psi_2'\psi(2) = u(b1)_{1s}u(b1)_{cs}u(a2)_{1s}u(a2)_{1s}\,,\\
G' &= \psi_2'\psi(3) = u(b1)_{1s}u(b1)_{1s}u(a2)_{1s}u(a2)_{cs}\,,\\
H' &= \psi_2'\psi(4) = u(b1)_{1s}u(a1)_{cs}u(a2)_{1s}u(b2)_{1s}
\end{aligned}\right\} \qquad (25)$$

We observe the following symmetry relations amongst their products By interchange of the nuclei '*a*' and '*b*', we pass from A to G, B to H, C to E and D to F By interchange of electrons 1 and 2 we pass from A to F, B to E, C to H, and D to G

It is found after some work (Note 1, p 103) that the integrals contained in (24) either vanish, or all reduce to a single integral, *viz*,

$$I = S\int u(a1)_{1s}u(b1)_{cs}(r_{a1}^2 - r_{b1}^2)d\Omega_1 \qquad (26)$$

One can evaluate this integral by the use of elliptic co-ordinates It has been shown (in Note 1) that

I = constant ×

$$\oint_{\xi}\int_{1}^{\infty}\int_{-1}^{1} \exp\left(-\frac{\lambda q}{2}(1+2\iota k\xi)\right) \exp\left(-\frac{\mu q}{2}(1-2\iota k\xi)\right)(\lambda+\mu)F(\xi)d\mu d\lambda d\xi$$

where $F(\xi) = (\xi+\frac{1}{2})^{-\iota n'-1}(\xi-\frac{1}{2})^{\iota n'-1}$, $n' = k^{-1} = \sqrt{\nu_0/(\nu-\nu_0)}$ and

$$\text{constant} = -\frac{\sqrt{2}}{16\pi}\frac{n'q^4S}{\sqrt{1-\exp(-2\pi n')}} \quad .. \quad (27)$$

The transitions which give values different from zero can easily be seen from the following grouping —

H_2	S	S	S	S	A	A	A	A
H_2^+ *e*	S^EA^N	S^ES^N	A^ES^N	A^EA^N	S^EA^N	S^ES^N	A^ES^N	A^EA^N
Tran Prob	4I	0	0	0	0	0	−4I	0

In the above, S against H_2 denotes S^ES^N or A^EA^N, and A against H_2 denotes S^EA^N or A^ES^N So that the only transitions which are non-zero are

$$S \text{ or } \begin{cases} S^NS^E \\ A^NA^E \end{cases} \text{ of } H_2 \longrightarrow S^FA^N \text{ of } H_2^+$$

$$A \text{ or } \begin{cases} A^ES^N \\ S^EA^N \end{cases} \text{ of } H_2 \longrightarrow S^NA^E \text{ of } H_2^+.$$

That is to say, transitions occur to antisymmetric states of H_2^+ only. The transition-probability is now given by

$$M^e_{kk'}(z) = 4CC_2eI/q \text{ or } 4C'C_3eI/q \qquad \ldots \quad \ldots \quad (28)$$

where I is given in (27)

So that the complete expression for $M^e_{kk'}(z)$ is

$$-\frac{1}{8\sqrt{1\pm S^2}}\;\frac{1}{\sqrt{1\pm X^2\mp SY}}\;\frac{n'q^3S}{\sqrt{1-\exp(-2\pi n')}}\cdot\frac{1}{4\pi}\oint\limits_{\xi}\int\limits_{1}^{\infty}\int\limits_{-1}^{1}\exp\left(-\tfrac{1}{2}\lambda q(1+2ik\xi)\right)$$

$$\exp\left(-\tfrac{1}{2}\mu q(1-2ik\xi)\right).\lambda\mu(\lambda+\mu)(\xi+\tfrac{1}{2})^{-in'-1}(\xi-\tfrac{1}{2})^{in'-1}d\xi d\lambda d\mu \quad \ldots \quad (29)$$

We have next to find out the values of X, Y and J, given by

$$X = \int u(a1)_{1s}u(b1)_{cs}\,d\Omega_1, \qquad\qquad Y = \int u(a1)_{cs}u(b1)_{cs}\,d\Omega_1;$$

$$J = \oint\int\int \exp\left(-\tfrac{1}{2}\lambda q(1+2ik\xi)\right)\exp\left(-\tfrac{1}{2}\mu q(1-2ik\xi)\right)\lambda\mu(\lambda+\mu).F(\xi)d\lambda d\mu d\xi,$$

where the value of $F(\xi)$ has been given *ante*

The solution of X is given in Note 2(*a*), p 105, and that of J, in Note 2(*b*), p 107 As regards Y we observe that if we replace $u(b, 1)_{cs}$ by $u(a, 1)_{cs}$ then the integral reduces to $\int[u(a1)_{cs}]^2\,d\Omega_1$ This integration cannot be carried out rigorously, for the exact ψ-function must be replaced by the asymptotic wave-function (vide Bethe, *Handbuch der Physik*, Vol 24) for the continuous state which holds for large distance from the nucleus This simplified function is then normalized for a small finite range of energy ΔE The asymptotic wave-function holds for distances where $1/r^2$ can be neglected in comparison with $1/r$ (*i e* $1/r \gg 1/r^2$) At such distances one can notice that r_{a1} and r_{b1} will be almost identical, for then q is very small compared to either of them. Hence we may replace r_{a1} for r_{b1} in the wave-function Thus the integral

$$Y = \int u(a1)_{cs}\,u(b1)_{cs}d\Omega_1 \qquad . \quad \ldots \quad (30)$$

can be given the asymptotic form $\simeq \int u(a1)_{cs}u(a1)_{cs}d\Omega_1$.

Since $u(a, 1)_{cs}$ is already the normalized eigen-function the integral Y has the value unity We have thus

$$M^e_{kk'}(z) = 2CC_2\,ek(2J)/q \text{ or } 2C'C_3\,ek(2J)/q$$

$$= -\frac{1}{\sqrt{1\pm S^2}}\cdot\frac{1}{\sqrt{1\pm X^2\mp S}}\cdot\frac{eq^3S}{32\pi}\cdot\frac{n'J}{\sqrt{1-\exp(-2\pi n')}} \quad \ldots \quad (31)$$

The evaluation of the integral J has been given in Note 2(*b*); so we quote here its value

$$J = \exp(-2n'\cot^{-1}n')\left[\frac{4\pi n'}{1+n'^2}\,G_1(q)+\frac{4\pi n'^3}{(1+n'^2)^2}\,G_2(q)\right] \quad \ldots \quad (32)$$

where $$G_1(q) = 8(1/q^2+6/q^4)\cosh q-24(1/q^3+8/q^5)\sinh q,$$
$$G_2(q) = -32(1/q^4\ \cosh q+1/q^5\ \sinh q).$$

The complete expression for the electronic transition probability is given below:

$$M^{e}_{kk'}(z) = -\frac{1}{\sqrt{1\pm S^2}}\cdot\frac{1}{\sqrt{1\pm X^2\mp S}}\cdot\frac{eS\exp(-2n'\cot^{-1}n')}{\sqrt{1-\exp(-2\pi n')}}\times$$
$$\times\left[\frac{n'^2}{1+n'^2}\left\{\left(q+\frac{6}{q}\right)\cosh q-3\left(1+\frac{2}{q^2}\right)\sinh q\right\}\right.$$
$$\left.+\left(\frac{n'^2}{1+n'^2}\right)^2\left\{-\frac{4}{q}\cosh q+\frac{4}{q^2}\sinh q\right\}\right]$$
$$= \frac{eS\exp(-2n'\cot^{-1}n')}{\sqrt{(1\pm S^2)(1\pm X^2\mp S)(1-\exp(-2\pi n'))}}\left[\left(\frac{\nu_0}{\nu}\right)\left\{\left(q+\frac{6}{q}\right)\cosh q\right.\right.$$
$$\left.\left.-3\left(1+\frac{2}{q^2}\right)\sinh q\right\}+\left(\frac{\nu_0}{\nu}\right)^2\left\{-\frac{4}{q}\cosh q+\frac{4}{q^2}\sinh q\right\}\right] \qquad (33)$$

where
$$S = (1+2q+q^2/3)\exp(-q),$$
$$X = -\frac{2n'^2}{1+n'^2}\sqrt{\frac{2}{1-\exp(-2\pi n')}}\left(\cosh q-\frac{1}{q}\sinh q\right)$$

Hence, for electronic transition, $\tau(\nu)$ is given by

$$\tau(\nu) = \frac{8\pi^3\nu}{c}\left|M^{e}_{kk'}\right|^2$$
$$= \frac{8\pi^3\nu e^2S^2\exp(-4n'\cot^{-1}n')}{c[(1\pm S^2)(1\pm X^2\mp S)(1-\exp\overline{-2\pi n'})]}\left\{\left(\frac{\nu_0}{\nu}\right)^2G_{11}^2(q)+2\left(\frac{\nu_0}{\nu}\right)^3G_{12}(q)\right.$$
$$\left.+\left(\frac{\nu_0}{\nu}\right)^4G_{22}^2(q)\right\} \qquad . \qquad (34)$$

where
$$\begin{cases} G_{11}(q) = (q+6/q)\cosh q-3(1+2/q^2)\sinh q, \\ G_{22}(q) = -4\cosh q/q+4\sinh q/q^2,\ G_{12}(q) = G_{11}(q)G_{22}(q), \\ \nu_0/\nu = n'^2/(1+n'^2),\ n' = \sqrt{\nu_0/(\nu-\nu_0)} \end{cases}$$

or

$$\tau(\nu) = \frac{8\pi^3\nu e^2S^2\exp(-4n'\cot^{-1}n')}{c[(1\pm S^2)(1\pm X^2\mp S)(1-\exp\overline{-2\pi n'})]}\left\{0{\cdot}777\left(\frac{\nu_0}{\nu}\right)-2{\cdot}2038\left(\frac{\nu_0}{\nu}\right)^2\right\} \quad .. \quad (34{\cdot}1)$$

for $q = 1{\cdot}418$, $\cosh q = 2{\cdot}17$ and $\sinh q = 1{\cdot}92$.

We can now compare the value of $\tau(\nu)$ for the electron-transition $1s^2 \rightarrow 1s\sigma s$ with that for the H-atom $1s \rightarrow \infty p$. For the last, we have according to Bethe (1936):

$$\tau(\nu) = \frac{2^8}{3}\frac{\pi e^2}{mc}\frac{\nu_0^3}{\nu^4}\frac{\exp(-4n'\cot^{-1}n')}{1-\exp(-2\pi n')}. \quad .. \quad . \quad (35)$$

For the threshold frequency, we have $\nu = \nu_0$ and

$$\tau_0 = \frac{2^8}{3} \frac{\pi e^2}{mc} \frac{\epsilon^{-4}}{\nu_0} = 1{\cdot}26 \times 10^{-17}\ cm^2.$$

For the electronic part of the molecular transition, we have, according to (34·1)

$$\tau(\nu) = \frac{8\pi^3 \nu e^2}{c} \frac{2a^3}{e^2} \left\{ \left(\frac{\nu_0}{\nu}\right) G_{11} + \left(\frac{\nu_0}{\nu}\right)^2 G_{22} \right\}^2 Q \qquad .. \quad (36)$$

Here we have written $\tau(\nu)$ in usual C G S units in place of Hartree units in which $\tau(\nu)$ in (34) has been expressed For this it has been necessary to multiply (34 1) by $2a^3/e^2$, where 'a' is the Bohr-radius, '2' representing the number of electrons capable of making the transition By 'Q' we denote the complicated expression —

$$\frac{S^2}{(1 \pm S^2)\,(1 \pm X^2 \mp S)} \; \frac{\exp\,(-4n' \cot^{-1} n')}{1 - \exp\,(-2\pi n')}.$$

Now it can be shown after some work that the above expression reduces to

$$\tau(\nu) = \frac{\pi e^2}{mc} \left(\frac{\nu_0}{\nu_1}\right)^2 \frac{1}{\nu_0} \left(G_{11} + \left(\frac{\nu_0}{\nu}\right) G_{22}\right)^2 Q, \qquad .. \quad (37)$$

where ν_1 = Rydberg frequency $= 2\pi^2 e^4 m/h^3$

This expression may be contrasted with (35) Let us compare their threshold values At $\nu = \nu_0$, we have for the ionization of H_2 to $H_2{}^+$

$$\tau_0 = \frac{\pi e^2}{mc} \left(\frac{\nu_0}{\nu_1}\right)^2 \frac{1}{\nu_0} \,(G_{11}+G_{22})^2\, \epsilon^{-4} \left\{ \frac{S^2}{(1+S^2)\,(1+X^2-S)} \right\} \qquad (38)$$

Now we have

$$(G_{11}+G_{22})^2 = (-1{\cdot}524)^2 = 2{\cdot}26,$$
$$S^2/(1+S^2)(1+X^2-S) = 1\ 233,$$
$$\nu_0/\nu_1 = 124569/109765 = 1{\cdot}135.$$

From these figures, we obtain for ionization of H_2

$$\tau_0 = \frac{\pi e^2}{mc} \frac{1}{\nu_1} \epsilon^{-4} [1\ 135 \times 1\ 233 \times 2\ 325] = (3\ 252) \frac{\pi e^2 \epsilon^{-4}}{mc\nu_1} \qquad (38\ 1)$$

We have, therefore, τ_0 for the process $H_2 \rightarrow H_2^+$ τ_0 for $H \rightarrow H^+ = 3\ 252$ $2^8/3 = 3{\cdot}8 \times 10^{-2}$, *i e*, the molecular process is nearly 25 times weaker

This is as is otherwise expected, for the process $1s^2 \rightarrow 1s\infty s$ should necessarily be rather feeble The main process would be from $1s^2 \rightarrow 1s\infty p$ The value of $\tau(\nu)$ for this process is very difficult to calculate, but it is being carried out, with no definite result to report at present Of course, this value of $\tau(\nu)$ for molecular ionization would be further reduced on account of the value of $M^2_{kk'}$ (vide *infra*).

4 TRANSITION-PROBABILITY DUE TO VIBRATION

Let us now calculate the vibrational part of $|M_{kk'}|$, *viz*,

$$\int \psi_1(V', q_1)\psi_2(V'', q_2)d\Omega_{v}.$$

Here $\psi_1(V', q_1)$ refers to the vibrational state of the H_2^+-molecule, V' being the quantum number of the particular vibrational state to which H_2^+ is raised by absorption of light We write $\psi_1(V', q_1)$ for H_2^+ ion, q_1 being the nuclear distance Similarly, $\psi_2(V'', q_2)$ refers to the H_2-molecule Now we have (vide Pauling and Wilson's 'Quantum Mechanics', 1935, p 107)

$$\psi_1(V', q_1) = N_{V'} \exp(-\beta_1 q_1^2/2) H_{V'}(\sqrt{\beta_1}q_1) \qquad . \quad (39)$$

where $q_1 = q - q_0'$, where q is the separation between the component nuclei, q_0' = normal distance between the nuclei in H_2^+, $\beta_1 = 4\pi^2\mu\omega_0'/h$, μ being the reduced mass (= M/2, M is the mass of the H-atom), ω_0' is the *fundamental* vibrational frequency of H_2^+ Further,

$$N_{V'} = \left[\frac{1}{2^{V'}\ V'!}\sqrt{\frac{\beta_1}{\pi}}\right]^{\frac{1}{2}} \qquad .. \quad . \quad (40)$$

In a similar way, it can be shown that

$$\psi_2(V'', q_2) = N_{V''} \exp(-\beta_2 q_2^2/2) \ \ H_{V''}(\sqrt{\beta_2}q_2) \qquad (41)$$

where $\beta_2 = 4\pi^2\mu\omega_0''/h$, $q_2 = q - q_0''$, q_0'' = separation between nuclei in H_2, and $N_{V''}$ has a value similar to (40) We then have

$$|M_{kk'}^{v}| = \int \psi_1(V', q_1)\psi_2(V'', q_2)dq \qquad (42)$$

The evaluation of integrals of type (42) has been carried out by Hutchisson (1930), but his expressions have been given in too much condensed form for any numerical calculation We therefore work out the integral (42) in detail

Let us put $\omega_0''/\omega_0' = \alpha^2$.

Further, as we have observed, since $q_2 = q - q_0''$, and $q_1 = q - q_0'$, where q is the running co-ordinate representing the distance between the nuclei, and q_0'', q_0' are the nuclear distances for H_2 and H_2^+, we have

$$q_2 = q_1 + q_0' - q_0''$$

and
$$\sqrt{\beta_2}q_2 = \sqrt{\beta_2}(q_1 + q_0' - q_0'') = \alpha\eta + \delta$$

where
$$\eta = \sqrt{\beta_1}q_1, \quad \delta = \sqrt{\beta_2}(q_0' - q_0'').$$

We have therefore for the integral (42) to denote here by the symbol $I_{V'V''}$:

$$I_{V'V''} = \left[\frac{1}{2^{V'+V''}.\ V'!\ V''!}\right]^{\frac{1}{2}}\left(\frac{4\pi\mu}{h}\right)^{\frac{1}{2}}(\omega_0'\omega_0'')^{\frac{1}{4}}\beta_1^{-\frac{1}{4}}\{I\}, \qquad .. \ (42{\cdot}1)$$

where

$$\{I\} = \int_{-\infty}^{\infty} \exp(-\tfrac{1}{2}\eta^2) \exp(-\tfrac{1}{2}(\alpha\eta + \delta)^2)\ H_{V'}(\eta)\ H_{V''}(\alpha\eta + \delta)\, d\eta. \quad .. \quad (43)$$

The occurrence of $\beta_1^{-\frac{1}{2}}$ in (42 1) is due to the fact that $d\Omega_v = dq$, and $dq = d\eta/\sqrt{\beta_1}$

After a little work, we obtain

$$I_{V'V''} = \left[\frac{\alpha/\pi}{2^{V'+V''}\ V'!\,V''!}\right]^{\frac{1}{2}}\{I\} \quad . \tag{44}$$

The integral $\{I\}$ has been worked out by Hutchisson, and it is useless to repeat the results We are concerned only with the case where $V'' = 0$ It can be shown after some work that

$$I_{00} = \sqrt{\frac{2\alpha}{1+\alpha^2}}\exp\left(-\delta^2/2\,(1+\alpha^2)\right) \tag{44·1}$$

and the ratios $I_{V'0}/I_{00}$ are shown in the following table

TABLE I

V''	V'	$I_{V'0}/I_{00}$
0	1	$\frac{1}{\sqrt{2}}d_1$
0	2	$\frac{1}{\sqrt{2}}(d_2+b_2)$
0	3	$\sqrt{\frac{3}{4}}(d_3+b_2d_1)$
0	4	$\sqrt{\frac{3}{2}}(d_4+b_2d_2+b_4)$
0	5	$\sqrt{\frac{15}{4}}(d_5+b_yd_3+b_4d_1)$
.		.
0	n	$\sqrt{\frac{n!}{2^{n/2}}}(d_n+b_2d_{n-2}+b_4d_{n-4}+\quad)$

where

$$d_x = \left(\frac{2\alpha x}{1+\alpha^2}\right)^x,\ b_y = \left(\frac{1-\alpha^2}{1+\alpha^2}\right)^{y/2},$$

y being even-numbered, and x any integral, even or odd

Numerical Calculation.

We have now

$$q_0'' = 0\,749\ \text{Å U.},\quad q_0' = 1{\cdot}070\ \text{Å.U},$$
$$\omega_0'' = 4275\ \text{cm}^{-1},\quad \omega_0' = 2235\ \text{cm}^{-1}.$$

Hence
$$\begin{aligned}\alpha &= (\omega_0''/\omega_0')^{\frac{1}{2}} = 1\ 3812 \\ &= \sqrt{\frac{4\pi^2\mu\omega_0''}{h}}\,(q_0'-q_0'') \\ &= 0\ 1221(q_0'-q_0'')(M\omega_0'')^{\frac{1}{2}},\end{aligned}$$
where q_0', q_0'' are expressed in Angstrom, M with O = 16, ω_0'' in cm^{-1}.

We easily verify that, for the present case, $\delta = 2\ 56$ With the aid of these values, we can calculate d_s and b_y and then calculate the numerical value of $I_{V''0}$, for integral values of V' These are shown in Tables (II) and (III)

We have further $I_{00} = 1\ 7552\times10^{-1}$

TABLE II

$b_0 = 1\ 00000$	$d_0 = 1\ 00000$	$d_5 = -0\ 68172$
$b_2 = -0\ 31210$	$d_1 = -2\ 41300$	$d_6 = 0\ 27416$
$b_4 = 0\ 04873$	$d_2 = 2\ 91130$	$d_7 = -0\ 09450$
$b_6 = -0\ 00606$	$d_3 = -2\ 34163$	$d_8 = 0\ 02850$
$b_8 = 0\ 00039$	$d_4 = 1\ 41260$	$d_9 = -0\ 00764$

TABLE III.

V''	V'	$I_{V'0}/I_{00} = M^v_{kk'}/I_{00}$	$M^v_{kk'}$	$\lvert M^v_{kk'}\rvert^2$
0	0	1 0000	$1\ 7552\times10^{-1}$	$3\ 0807\times10^{-2}$
0	1	−1 7113	$-3\ 0037\times10^{-1}$	$9\ 0222\times10^{-2}$
0	2	1 8381	$3\ 2262\times10^{-1}$	$10\ 4084\times10^{-2}$
0	3	−1 3757	$-2\ 4146\times10^{-1}$	$5\ 8303\times10^{-2}$
0	4	0 6769	$1\ 1881\times10^{-1}$	$1\ 4116\times10^{-2}$
0	5	−0 1325	$-0\ 2326\times10^{-1}$	$0\ 0541\times10^{-2}$
0	6	−0 1039	$-0\ 1824\times10^{-1}$	$0\ 0333\times10^{-2}$
0	7	0 1178	$0\ 2068\times10^{-1}$	$0\ 0428\times10^{-2}$
0	8	−0·0744	$-0\ 1306\times10^{-1}$	$0\ 0171\times10^{-2}$

5 CONCLUSION

We can now get a qualitative idea regarding the nature of the complete absorption curve $\tau(\nu)/\nu$. Referring back to (2), (6), (34·1) and (44), and putting $[\int\psi_1(m)\psi_2(m)d\phi]^2$ equal to unity, as can be easily verified, we have

$$\tau_\nu^+ = \frac{8\pi^3e^2\nu_0}{c}\,\mathrm{L}(\nu)F(\mathrm{X},\,\mathrm{S})\Phi^2(\nu)\mathrm{I}^2_{V'V''},$$

$$\tau_\nu^- = \frac{8\pi^3e^2\nu_0}{c}\,\mathrm{L}(\nu)F^*(\mathrm{X},\,\mathrm{S})\Phi^2(\nu)\mathrm{I}^2_{V'V''},$$

where $\mathrm{L}(\nu)$, $F(\mathrm{X}, \mathrm{S})$, $F^*(\mathrm{X}, \mathrm{S})$, $\Phi(\nu)$ are quantities defined in Tables IV to X given in the Appendix.

We observe from the tables (VII), (VIII), that $F(\mathrm{X}, \mathrm{S})$, $F^*(\mathrm{X}, \mathrm{S})$ are slowly varying functions. When $\nu = \nu_0$, $F(\mathrm{X}, \mathrm{S}) = 1{\cdot}2330$, when $\nu = 2\nu_0$, it is 1·3150. But we have, in practice, to plot the $\tau(\nu)/\nu$ curve close to $\nu = \nu_0$; hence it is convenient to take this quantity as constant, say 1·25. Similarly, $1-\exp(-2\pi n')$ also varies slowly for this region. The main variation is in $\Phi(\nu)$. We observe that $\Phi(\nu)$ becomes zero at a certain frequency near $\nu = 3\nu_0$, and after that slowly rises. This is a somewhat unexpected result, but in actual practice we have not to go so far, because absorption will be mostly confined to the neighbourhood of $\nu = \nu_0$.

Since $\nu = \nu_e + (V'+\frac{1}{2})\omega_0' - (V''+\frac{1}{2})\omega_0''$, neglecting rotation, and since $V'' = 0$, we have $\nu = 123569 + \frac{1}{2}(\omega_0' - \omega_0'') + V'\omega_0' = \nu_0 + \omega_0'V' = 123549 + \omega_0'V'$. We get then $\nu_0 = 123549$, and the stretch from $\nu = \nu_0$ to $\nu = 2\nu_0$ contains about 56 ω_0'. We shall see presently, since the value of $\mathrm{I}_{V'0}$ jumps suddenly at each point $\nu = \nu_0 + \omega_0'V'$, where $V' = 1, 2, 3,$, and after $V' = 3$, the value of $\mathrm{I}_{V'0}$ drops suddenly, the possible zero value of $\Phi(\nu)$ at $\nu = 3\nu_0$ roughly is far outside the region we are contemplating. The actual calculations are shown in Table X, and finally in Table XI, and the form of the $\tau(\nu)/\nu$-curve is represented in Fig. 2.

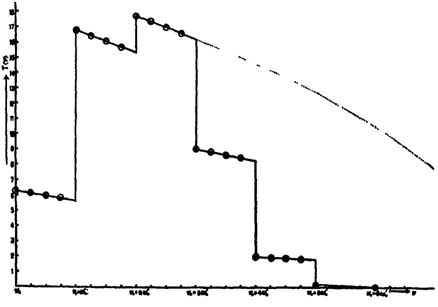


FIG. 2.

We observe from this, that the absorption curve behaves exactly in the way mentioned at the end of §1 The maximum value of $\tau(\nu)$ is not reached at $\nu = \nu_0$, but at $\nu = \nu_0+2\omega_0'$, where it is about three times larger than the value at $\nu = \nu_0$ At each vibrational number there is a sudden jump, *up* before $\nu = \nu_0+2\omega_0'$ and *down* after $\nu = \nu_0+2\omega_0'$ It therefore appears that after $\nu = \nu_0+3\omega_0'$, the continuous absorption, which raises H_2^+ to the third vibrational level, and leaves the rest of the energy to the electron, is more probable than raising H_2^+ to a higher vibrational level So this part of the curve is drawn up to some distance and is shown by dots

As the actual absorption curve $\tau(\nu)/\nu$ leading to photo-dissociation will correspond to the process $1s^2 \rightarrow 1s\infty p$ no attempt has been made to obtain further conclusions, particularly as the experimental results are very meagre

Lastly, we have great pleasure in acknowledging our gratefulness to Prof M N Saha, F R S, for his inspiring guidance and the keen interest he has shown in the several stages of this work

Note 1

To show that the various integrals contained in

$$M(z) = \frac{CC_1e}{q}\int\int(\psi_1'+\psi_2')[(r_{a1}^2-r_{b1}^2)+(r_{a2}^2-r_{b2}^2)] \times$$
$$\times(\psi(1)+\psi(2)+\psi(3)+\psi(4))d\Omega_1\, d\Omega_2$$

either reduce to zero or to the form

$$I = S\int u(a1)_{1s}\, u(b1)_{cs}\,(r_{a1}^2-r_{b1}^2)\, d\Omega_1$$

We take each of the products in (25) and multiply by the electric moment $[M(z_1)+M(z_2)]$ and integrate over the co-ordinate spaces of the electrons

Since A and G differ only in an interchange of nuclei, the integrals obtained from the product of the electric moment and A or G will be either equal, or equal except for a change of sign, according as there is, or is not, a change in the nuclear symmetry during the transition A similar argument holds for an interchange of electrons as between A and F, and D and G This shows that the expressions A, D, F and G when integrated after multiplication with the electric moment will have the same absolute value In an exactly similar manner it may be concluded that B, H, C and E will have the same absolute value It is presently shown that the integral $\int A[M]d\Omega = 0$ Hence the integrals obtained from D, F and G are also zero

$$\int A[M]d\Omega = \int\psi_1'\psi(1)\,[M(z_1)+M(z_2)]d\Omega$$
$$= \int u(b2)_{1s}\, u(b2)_{cs}\, d\Omega_2 \quad \int u(a1)_{1s}(r_{a1}^2-r_{b1}^2)\, u(a1)_{1s} d\Omega_1$$
$$+ \int[u(a1)_{1s}]^2\, d\Omega_1 \quad \int u(b2)_{1s}\,(r_{a2}^2-r_{b2}^2)\, u(b2)_{cs}\, d\Omega_2$$

Remembering $\int u(b2)_{1s}\, u(b2)_{cs} = 0$, due to orthogonality, and using elliptic co-ordinates defined by

$$\lambda = (r_{a2}+r_{b2})/q,\ \mu = (r_{a2}-r_{b2})/q,\ d\Omega = \tfrac{1}{8}\, q^3(\lambda^2-\mu^2)d\lambda\, d\mu\, d\phi,$$

we get

$$u(b2)_{1s} = \frac{1}{\sqrt{\pi}} \exp\left(-\tfrac{1}{2}q(\lambda-\mu)\right),$$

and

$$u(b2)_{cs} = -\sqrt{\frac{2}{1-\epsilon^{-2\pi n'}}}\ \frac{n'}{q(\lambda-\mu)}\ \frac{1}{2\pi}\oint_{\xi} \exp\left(-\iota qk\xi(\lambda-\mu)\right)F(\xi)d\xi$$

The integral now assumes the form

$$\text{Const} \oint_{\xi}\int_{1}^{\infty}\int_{-1}^{1} \exp\left(-\tfrac{1}{2}\lambda q(1+2\iota k\xi)\right) \exp\left(\tfrac{1}{2}\mu q(1+2\iota k\xi)\right) \times$$

$$\times \lambda\mu(\lambda+\mu)(\xi+\tfrac{1}{2})^{-\iota n'-1}(\xi-\tfrac{1}{2})^{\iota n'-1}\, d\xi\, d\lambda\, d\mu$$

A factor of the above integral is the following.—

$$\int_{1}^{\infty}\int_{-1}^{1} \lambda\mu(\lambda+\mu) \exp\left(-\tfrac{1}{2}\lambda q(1+2\iota k\xi)\right) \exp\left(\tfrac{1}{2}\mu q(1+2\iota k\xi)\right) d\lambda\, d\mu,$$

whose value is $4/q^2(1+2\iota k\xi)^2$, for this $=$ A′B′+C′D′,
where

$$A' = \int_{1}^{\infty} \lambda^2 \exp(-\lambda a)d\lambda = \epsilon^{-a}(1/a+2/a^2+2/a^3),\ (a = \tfrac{1}{2}q(1+2\iota k\xi))$$

$$B' = \int_{-1}^{1} \mu \exp(\mu a)d\mu = (\epsilon^{a}+\epsilon^{-a})/a-(\epsilon^{a}-\epsilon^{-a})/a^2,$$

$$C' = \int_{1}^{\infty} \lambda \exp(-\lambda a)d\lambda = \epsilon^{-a}(1/a+1/a^2),$$

$$D' = \int_{-1}^{1} \mu^2 \exp(\mu a)d\mu = (\epsilon^{a}-\epsilon^{-a})/a-2[(\epsilon^{a}+\epsilon^{-a})/a-(\epsilon^{a}-\epsilon^{-a})/a^2]/a$$

Hence the integral reduces to a contour integral

$$\text{Constant} \times \frac{4}{q^2}\oint_{\xi} (\xi+\tfrac{1}{2})^{-\iota n'-1}(\xi-\tfrac{1}{2})^{\iota n'-1}(1+2\iota k\xi)^{-2}d\xi,$$

with a pole at $\xi = \iota/2k$ The value of this $= 0$ (See Note 2(b))

Thus integrals A, D, F and G all vanish

We now take the integrals obtained from B, C, E and H One can show by multiplying out and evaluating that

$$\int B[M]d\Omega = -\int C[M]d\Omega = \int E[M]d\Omega = -\int H[M]d\Omega$$

Taking first the integral with B we get.—

$$\int \psi_1'\psi(2)[\mathrm{M}(z_1)+\mathrm{M}(z_2)]d\Omega$$

$$= \int u(a1)_{1s}u(b1)_{cs}(r_{1a}^2-r_{b1}^2)\,d\Omega_1 \int u(a2)_{1s}u(b2)_{1s}d\Omega_2 +$$

$$\int u(a1)_{1s}u(b1)_{cs}d\Omega_1 \int u(a2)_{1s}u(b2)_{1s}(r_{a2}^2-r_{b2}^2)\,d\Omega_2$$

Transforming

$$\int u\,(a2)_{1s}(r_{a2}^2 - r_{b2}^2)u(b2)_{1s}d\Omega_2$$

into elliptic co-ordinates defined above, we get it equivalent to

$$\frac{q^5}{8\pi}\int_0^{2\pi}\int_1^{\infty}\int_{-1}^{1}\lambda\mu(\lambda^2-\mu^2)\exp\left(-\tfrac{1}{2}q(\lambda+\mu)\right)\exp\left(-\tfrac{1}{2}q(\lambda-\mu)\right)d\lambda\,d\mu\,d\phi$$

$$= \frac{q^5}{4}\int_1^{\infty}\int_{-1}^{1}\lambda\mu\,(\lambda^2-\mu^2)\exp\,(-q\lambda)\,d\lambda d\mu = \frac{q^5}{4}\,[\mathrm{A''B''}-\mathrm{C''D''}] = 0,$$

for

$$\mathrm{A''} = \int_1^{\infty}\lambda^3\exp\,(-q\lambda)\,d\lambda = \epsilon^{-q}\,(1/q+3/q^2+6/q^3+6/q^4)\,,$$

$$\mathrm{B''} = \int_{-1}^{1}\mu d\mu = 0\,;$$

$$\mathrm{C''} = \int_1^{\infty}\lambda\exp\,(-q\lambda)\,d\lambda = \epsilon^{-q}\,(1/q+1/q^2)\,,$$

$$\mathrm{D''} = \int_{-1}^{1}\mu^3 d\mu = 0$$

Now

$$\int u\,(a2)_{1s}u\,(b2)_{1s}\,d\Omega_2$$

is our Suguira-integral S.

Hence the integral containing B

$$= \mathrm{S}\int u\,(a1)_{1s}(r_{a1}^2-r_{b1}^2)\,u\,(b1)_{cs}\,d\Omega_1 = \mathrm{SI^*} = \mathrm{I}$$

From E we have similarly a value = I; and from each of C and H the value −I.

Note 2(a)

To evaluate

$$\mathrm{X} = \int u\,(a1)_{1s}u\,(b1)_{cs}\,d\Omega_1$$

We have (See Bethe, *Handbuch der Physik*, Bd 24, 1933, l c)

$$u\,(a1)_{1s} = \frac{1}{\sqrt{\pi}} \exp\,(-r_{a1})\,,$$

$$u\,(b1)_{cs} = -\sqrt{\frac{2}{1-\epsilon^{-2\pi n'}}}\,\frac{1}{2^3\pi^{\frac{1}{2}}}\,\frac{n'}{r_{b1}} \oint_{\xi} \exp\,(-2\iota k r_{b1}\xi)\, F(\xi)\, d\xi$$

Transforming into elliptic co-ordinates the above eigen-functions become

$$u\,(a1)_{1s} = \frac{1}{\sqrt{\pi}} \exp\left(\frac{-q}{2}\,(\lambda+\mu)\right),$$

$$u\,(b1)_{rs} = -\frac{1}{\sqrt{1-\epsilon^{-2\pi n'}}}\;\frac{n'}{\pi^{\frac{3}{2}}\;2^{\frac{1}{2}}}\;\frac{1}{q\,(\lambda-\mu)} \oint_{\xi} \exp\,(-\iota kq\,(\lambda-\mu)\,\xi)\quad F(\xi)\, d\xi$$

The integral X now takes the form

$$\mathrm{X} = -\frac{n'q^2}{16\pi}\sqrt{\frac{2}{1-\epsilon-2\pi n'}} \oint_{\xi}\int_{1}^{\infty}\int_{-1}^{1} \exp\,(-\tfrac{1}{2}\lambda q(1+2\iota k\xi))\times$$
$$\times \exp\,(-\tfrac{1}{2}\mu q(1-2\iota k\xi))\quad (\lambda+\mu)F(\xi)d\lambda\, d\mu\, d\xi$$

Let us evaluate

$$\mathrm{J}' = \oint_{\xi}\int_{1}^{\infty}\int_{-1}^{1} \exp\,(-\tfrac{1}{2}\lambda q(1+2\iota k\xi))\, \exp\,(-\tfrac{1}{2}\mu q(1-2\iota k\xi))\quad (\lambda+\mu)\; F(\xi)\; d\lambda\, d\mu\, d\xi$$

Call $\mathrm{J}'' = \int_{1}^{\infty}\int_{-1}^{1} \exp\,(-a\lambda)\, \exp\,(-b\mu)\quad (\lambda+\mu)\; d\lambda\, d\mu,$

where

$$a = \tfrac{1}{2}q\,(1+2\iota k\xi),\quad b = \tfrac{1}{2}q\,(1-2\iota k\xi)$$

$$\mathrm{J}'' = (\epsilon^{b}-\epsilon^{-b})\,\{\mathrm{I}\}/b + \epsilon^{-a}\,\{\mathrm{III}\}/a\,,$$

where

$$\{\mathrm{I}\} = \int_{1}^{\infty} \lambda \exp\,(-a\lambda)\; d\lambda = \epsilon^{-a}\,(1/a+1/a^2)\,,$$

$$\{\mathrm{III}\} = \int_{-1}^{1} \mu \exp\,(-b\mu)\; d\mu = \epsilon^{b}\,(-1/b+1/b^2) - \epsilon^{-b}(1/b+1/b^2)$$

Whence

$$\begin{aligned}\mathrm{J}'' &= \epsilon^{-(a-b)}\quad (1/a^2b+1/ab^2) - \epsilon^{-(a+b)}\quad (2/ab+1/a^2b+1/ab^2)\\ &= \epsilon^{-2q\iota k\xi}\,[8/q^3(1+2\iota k\xi)^2(1-2\iota k\xi)+8/q^3(1+2\iota k\xi)(1-2\iota k\xi)^2]\\ &\qquad - \epsilon^{-q}\,[8/q^2(1+2\iota k\xi)(1-2\iota k\xi)+8/q^3(1+2\iota k\xi)^2(1-2\iota k\xi)\\ &\qquad + 8/q^3(1+2\iota k\xi)(1-2\iota k\xi)^2]\,.\end{aligned}$$

Splitting up into partial fractions (see a list in the body of Note 2(b)) and rearranging we get

$$\begin{aligned} \mathrm{J}' = h_1 \oint_\xi (1+2\iota k\xi)^{-1} F(\xi)d\xi + h_{-1} \oint_\xi (1-2\iota k\xi)^{-1} F(\xi)d\xi + h_2 \oint_\xi (1+2\iota k\xi)^{-2} F(\xi)d\xi \\ + h_{-2} \oint_\xi (1-2\iota k\xi)^{-2} F(\xi)d\xi + h_1' \oint_\xi (1+2\iota k\xi)^{-1} F(\xi) \exp(-2q\iota\xi/n')d\xi \\ + h'_{-1} \oint_\xi (1-2\iota k\xi)^{-1} F(\xi) \exp(-2q\iota\xi/n')d\xi \\ + h_2' \oint_\xi (1+2\iota k\xi)^{-2} F(\xi) \exp(-2q\iota\xi/n')\, d\xi \\ + h'_{-2} \oint_\xi (1-2\iota k\xi)^{-2} F(\xi) \exp(-2q\iota\xi/n')\, d\xi, \end{aligned}$$

where

$$\begin{aligned} h_1 &\equiv h_{-1} = -4\epsilon^{-q}(1/q^2+1/q^3), \\ h_2 &\equiv h_{-2} = -4\epsilon^{-q}/q^3, \\ h_1' &\equiv h'_{-1} = 4/q^3, \\ h_2' &\equiv h'_{-2} = 4/q^3 \end{aligned}$$

Quoting the values of the contour integrals (given in Note 2(*b*)) we derive after simplifications —

$$\mathrm{J}' = \frac{32\pi n'}{1+n'^2} (\cosh q/q^2 - \sinh q/q^3) \exp(-2n' \cot^{-1} n'),$$

$$\mathrm{X} = -\frac{2n'^2}{1+n'^2} \sqrt{\frac{2}{1-\epsilon^{-2\pi n'}}} (\cosh q - \sinh q/q) \exp(-2n' \cot^{-1} n')$$

Note 2(*b*)

To evaluate

$$\mathrm{J} = \oint_\xi \int_1^\infty \int_{-1}^1 \exp(-\tfrac{1}{2}\lambda q(1+2\iota k\xi)) \exp(-\tfrac{1}{2}\mu q(1-2\iota k\xi)) \;\lambda\mu(\lambda+\mu) \times \\ \times F(\xi)\, d\lambda\, d\mu\, d\xi,$$

where $F(\xi) = (\xi+\tfrac{1}{2})^{-\iota n'-1}(\xi-\tfrac{1}{2})^{\iota n'-1}, \quad (k = 1/n')$

Call $\mathrm{J}_1 = \int_1^\infty (\lambda^2\mu+\lambda\mu^2) \exp(-\tfrac{1}{2}q\lambda(1+2\iota k\xi))\, d\lambda = \mu^2\{\mathrm{I}\}+\mu\{\mathrm{II}\},$

where $\{\mathrm{I}\} = \int_1^\infty \lambda \exp(-a\lambda)\, d\lambda = \epsilon^{-a}(1/a+1/a^2), \quad a = \tfrac{1}{2}q(1+2\iota k\xi)$

$$\{\mathrm{II}\} = \int_1^\infty \lambda^2 \exp(-a\lambda)\, d\lambda = \epsilon^{-a}(1/a+2/a^2+2/a^3).$$

Next, call $$J_2 = \int_{-1}^{1}[\mu^2\{\mathrm{I}\}+\mu\{\mathrm{II}\}]\exp(-b\mu)d\mu\,,\; b=\tfrac{1}{2}q(1-2ik\xi)$$

$$= \{\mathrm{I}\}\times\{\mathrm{IV}\}+\{\mathrm{II}\}\times\{\mathrm{III}\},$$

where $$\{\mathrm{III}\} = \int_{-1}^{1}\mu\exp(-b\mu)d\mu = \epsilon^{b}(-1/b+1/b^2)-\epsilon^{-b}(1/b+1/b^2)\,,$$

$$\{\mathrm{IV}\} = \int_{-1}^{1}\mu^2\exp(-b\mu)d\mu$$

$$= \epsilon^{b}(1/b-2/b^2+2/b^3)-\epsilon^{-b}(1/b+2/b^2+2/b^3)$$

$$J_2 = -\epsilon^{-(a+b)}[2/ab+3/a^2b+3/ab^2+4/a^2b^2+2/a^3b+2/ab^3+2/a^2b^3+2/a^3b^2]$$
$$+\epsilon^{-(a-b)}[-1/a^2b-1/ab^2+2/ab^3-2/a^3b+2/a^2b^3+2/a^3b^2]$$

Since $a+b=q$, $a-b=2qik\xi$, we write the expression for J_2 in full, thus

$$\begin{aligned}J_2 = -\epsilon^{-q}[&8/q^2(1+2ik\xi)(1-2ik\xi)+24/q^3(1+2ik\xi)^2(1-2ik\xi)\\ &+24/q^3(1+2ik\xi)(1-2ik\xi)^2+64/q^4(1+2ik\xi)^2(1-2ik\xi)^2\\ &+32/q^4(1+2ik\xi)^3(1-2ik\xi)+32/q^4(1+2ik\xi)(1-2ik\xi)^3\\ &+64/q^5(1+2ik\xi)^2(1-2ik\xi)^3+64/q^5(1+2ik\xi)^3(1-2ik\xi)^2]\\ &+\epsilon^{-2qik\xi}[-8/q^3(1+2ik\xi)^2(1-2ik\xi)-8/q^3(1+2ik\xi)(1-2ik\xi)^2\\ &-32/q^4(1+2ik\xi)^3(1-2ik\xi)+32/q^4(1+2ik\xi)(1-2ik\xi)^3\\ &+64/q^5(1+2ik\xi)^2(1-2ik\xi)^3+64/q^5(1+2ik\xi)^3(1-2ik\xi)^2]\end{aligned}$$

Next we shall have to split up each term into partial fractions We write down below the results of splitting up, putting $x=2ik\xi$ for short —

$f_0=1/(1+x)(1-x) \;=\tfrac{1}{2}/(1+x)+\tfrac{1}{2}/(1-x)\,,$

$f_1=1/(1+x)^2(1-x) \;=\tfrac{1}{2}/(1+x)^2+\tfrac{1}{4}/(1+x)+\tfrac{1}{4}/(1-x)\,,$

$f_2=1/(1+x)(1-x)^2 \;=\tfrac{1}{2}/(1-x)^2+\tfrac{1}{4}/(1-x)+\tfrac{1}{4}/(1+x)\,,$

$f_3=1/(1+x)^3(1-x) \;=\tfrac{1}{2}/(1+x)^3+\tfrac{1}{4}/(1+x)^2+\tfrac{1}{8}/(1+x)+\tfrac{1}{8}/(1-x)\,,$

$f_4=1/(1+x)(1-x)^3 \;=\tfrac{1}{2}/(1-x)^3+\tfrac{1}{4}/(1-x)^2+\tfrac{1}{8}/(1-x)+\tfrac{1}{8}/(1+x)\,,$

$f_5=1/(1+x)^3(1-x)^2=\tfrac{1}{4}/(1+x)^3+\tfrac{1}{4}/(1+x)^2+\tfrac{3}{16}(1+x)+\tfrac{1}{8}/(1-x)^2+\tfrac{3}{16}/(1-x)\,,$

$f_6=1/(1+x)^2(1-x)^3=\tfrac{1}{4}/(1-x)^3+\tfrac{1}{4}/(1-x)^2+\tfrac{3}{16}/(1-x)+\tfrac{1}{8}/(1+x)^2+\tfrac{3}{16}/(1+x),$

$f_7=1/(1+x)^2(1-x)^2=\tfrac{1}{4}/(1+x)^2+\tfrac{1}{4}/(1+x)+\tfrac{1}{4}/(1-x)^2+\tfrac{1}{4}/(1-x)$

Utilizing these equivalent expressions for $f_0, f_1,$ in the expression for J_2 we can write it in full thus

$$\begin{aligned}J_2 = -\epsilon^{-q}\Bigg[&\frac{1}{q^2}\left(\frac{4}{(1+x)}+\frac{4}{(1-x)}\right)+\frac{1}{q^3}\left(\frac{12}{(1+x)^2}+\frac{6}{(1+x)}+\frac{6}{(1-x)}\right)\\ &+\frac{1}{q^3}\left(\frac{12}{(1-x)^2}+\frac{6}{(1-x)}+\frac{6}{(1+x)}\right)+\frac{1}{q^4}\left(\frac{16}{(1+x)^2}+\frac{16}{(1+x)}+\frac{16}{(1-x)^2}+\frac{16}{(1-x)}\right)\\ &+\frac{1}{q^4}\left(\frac{16}{(1+x)^3}+\frac{8}{(1+x)^2}+\frac{4}{(1+x)}+\frac{4}{(1-x)}\right)\end{aligned}$$

$$+\frac{1}{q^4}\left(\frac{16}{(1-x)^3}+\frac{8}{(1-x)^2}+\frac{4}{(1-x)}+\frac{4}{(1+x)}\right)$$

$$+\frac{1}{q^5}\left(\frac{16}{(1-x)^3}+\frac{16}{(1-x)^2}+\frac{12}{(1-x)}+\frac{8}{(1+x)^2}+\frac{12}{(1+x)}\right)$$

$$+\frac{1}{q^5}\left(\frac{16}{(1+x)^3}+\frac{16}{(1+x)^2}+\frac{12}{(1+x)}+\frac{8}{(1-x)^2}+\frac{12}{(1-x)}\right)\Bigg]$$

$$+\epsilon^{-2q\iota k\xi}\Bigg[-\frac{1}{q^3}\left(\frac{4}{(1+x)^2}+\frac{2}{(1+x)}+\frac{2}{(1-x)}\right)$$

$$-\frac{1}{q^3}\left(\frac{4}{(1-x)^2}+\frac{2}{(1-x)}+\frac{2}{(1+x)}\right)$$

$$-\frac{1}{q^4}\left(\frac{16}{(1+x)^3}+\frac{8}{(1+x)^2}+\frac{4}{(1+x)}+\frac{4}{(1-x)}\right)$$

$$+\frac{1}{q^4}\left(\frac{16}{(1-x)^3}+\frac{8}{(1-x)^2}+\frac{4}{(1-x)}+\frac{4}{(1+x)}\right)$$

$$+\frac{1}{q^5}\left(\frac{16}{(1-x)^3}+\frac{16}{(1-x)^2}+\frac{12}{(1-x)}+\frac{8}{(1+x)^2}+\frac{12}{(1+x)}\right)$$

$$+\frac{1}{q^5}\left(\frac{16}{(1+x)^3}+\frac{16}{(1+x)^2}+\frac{12}{(1+x)}+\frac{8}{(1-x)^2}+\frac{12}{(1-x)}\right)\Bigg]$$

Rearranging above we get finally —

$$J_2 = [g_1/(1+2\iota k\xi)+g_{-1}/(1-2\iota k\xi)+g_2/(1+2\iota k\xi)^2+g_{-2}/(1-2\iota k\xi)^2$$
$$+g_3/(1+2\iota k\xi)^3+g_{-3}/(1-2\iota k\xi)^3]+\exp(-2q\iota k\xi)\,[g_1'/(1+2\iota k\xi)+g'_{-1}/(1-2\iota k\xi)$$
$$+g_2'/(1+2\iota k\xi)^2+g'_{-2}/(1-2\iota k\xi)^2+g_3'/(1+2\iota k\xi)^3+g'_{-3}/(1-2\iota k\xi)^3],$$

where

$$g_1 \equiv g_{-1} = -\epsilon^{-q}(4/q^2+12/q^3+24/q^4+24/q^5),$$
$$g_2 \equiv g_{-2} = -\epsilon^{-q}(12/q^3+24/q^4+24/q^5),$$
$$g_3 \equiv g_{-3} = -\epsilon^{-q}(16/q^4+16/q^5),$$
$$g_1' \equiv g_{-1}' = -4/q^3+24/q^5,$$
$$g_2' = -4/q^3-8/q^4+24/q^5,$$
$$g'_{-2} = -4/q^3+8/q^4+24/q^5,$$
$$g_3' = -16/q^4+16/q^5,\ g'_{-3} = 16/q^4+16/q^5$$

The integral J now splits up into twelve contour integrals —

$$J = g_1\oint_{\xi}\frac{F(\xi)d\xi}{(1+2\iota k\xi)}+g_{-1}\oint_{\xi}\frac{F(\xi)d\xi}{(1-2\iota k\xi)}+g_2\oint_{\xi}\frac{F(\xi)d\xi}{(1+2\iota k\xi)^2}+g_{-2}\oint_{\xi}\frac{F(\xi)d\xi}{(1-2\iota k\xi)^2}$$
$$+g_3\oint_{\xi}\frac{F(\xi)d\xi}{(1+2\iota k\xi)^3}+g_{-3}\oint_{\xi}\frac{F(\xi)d\xi}{(1-2\iota k\xi)^3}+g_1'\oint_{\xi}\frac{H(\xi)d\xi}{(1+2\iota k\xi)}+g'_{-1}\oint_{\xi}\frac{H(\xi)d\xi}{(1-2\iota k\xi)}$$
$$+g_2'\oint_{\xi}\frac{H(\xi)d\xi}{(1+2\iota k\xi)^2}+g'_{-2}\oint_{\xi}\frac{H(\xi)d\xi}{(1-2\iota k\xi)^2}+g_3'\oint_{\xi}\frac{H(\xi)d\xi}{(1+2\iota k\xi)^3}+g'_{-3}\frac{H(\xi)d\xi}{(1-2\iota k\xi)^3}$$

$$[H(\xi) \equiv \exp(-2q\iota k\xi)F(\xi)]$$

Since $(1+2\iota k\xi) = \frac{2\iota}{n'}(\xi-\tfrac{1}{2}\iota n')$ and $(1-2\iota k\xi) = -\frac{2\iota}{n'}(\xi+\tfrac{1}{2}\iota n')$, we get two types of contour integrals in the complex ξ-plane

1st type Branch points at $\xi = \pm\tfrac{1}{2}$, Pole at $\xi = +\tfrac{1}{2}\iota n'$
2nd type Branch points at $\xi = \pm\tfrac{1}{2}$, Pole at $\xi = -\tfrac{1}{2}\iota n'$

In the following list of values for the above integrals, the final results have been obtained by using Cauchy's theorem involving calculations of residues, *viz*

$$f(z) = \frac{1}{2\pi\iota}\oint_{\zeta}\frac{f(\zeta)d\zeta}{(\zeta-z)}, \qquad f'(z) = \frac{1}{2\pi\iota}\oint_{\zeta}\frac{f(\zeta)d\zeta}{(\zeta-z)^2},$$

$$f''(z) = \frac{2}{2\pi\iota}\oint_{\zeta}\frac{f(\zeta)d\zeta}{(\zeta-z)^3}, \qquad f^{n}(z) = \frac{n!}{2\pi\iota}\oint_{\zeta}\frac{f(\zeta)d\zeta}{(\zeta-z)^{n+1}}$$

$$(1) \quad \oint_{\xi}\frac{F(\xi)d\xi}{(1+2\iota k\xi)} = -\frac{4\pi n'}{(1+n'^2)}\exp(-2n'\cot^{-1}n'),$$

$$(2) \quad \oint_{\xi}\frac{F(\xi)d\xi}{(1-2\iota k\xi)} = \frac{4\pi n'}{(1+n'^2)}\exp(2n'\cot^{-1}n'),$$

$$(3) \quad \oint_{\xi}\frac{F(\xi)d\xi}{(1+2\iota k\xi)^2} = 0,$$

$$(4) \quad \oint_{\xi}\frac{F(\xi)d\xi}{(1-2\iota k\xi)^2} = \frac{16\pi n'^3}{(1+n'^2)^2}\exp(2n'\cot^{-1}n'),$$

$$(5) \quad \oint_{\xi}\frac{F(\xi)d\xi}{(1+2\iota k\xi)^3} = \frac{4\pi n'^3}{(1+n'^2)^2}\exp(-2n'\cot^{-1}n'),$$

$$(6) \quad \oint_{\xi}\frac{F(\xi)d\xi}{(1-2\iota k\xi)^3} = \frac{4\pi n'^3(11n'^2-1)}{(1+n'^2)^3}\exp(2n'\cot^{-1}n'),$$

$$(7) \quad \oint_{\xi}\frac{H(\xi)d\xi}{(1+2\iota k\xi)} = \frac{-4\pi n'}{(1+n'^2)}\exp(q-2n'\cot^{-1}n'),$$

$$(8) \quad \oint_{\xi}\frac{H(\xi)d\xi}{(1-2\iota k\xi)} = \frac{4\pi n'}{(1+n'^2)}\exp(-q+2n'\cot^{-1}n'),$$

$$(9) \quad \oint_{\xi}\frac{H(\xi)d\xi}{(1+2\iota k\xi)^2} = \frac{4\pi n'q}{(1+n'^2)}\exp(q-2n'\cot^{-1}n'),$$

$$(10) \quad \oint_{\xi}\frac{H(\xi)d\xi}{(1-2\iota k\xi)^2} = \left(\frac{4\pi n'q}{(1+n'^2)}+\frac{16\pi n'^3}{(1+n'^2)^2}\right)\exp(-q+2n'\cot^{-1}n'),$$

$$(11) \quad \oint_{\xi}\frac{H(\xi)d\xi}{(1+2\iota k\xi)^3} = \left(\frac{4\pi n'^3}{(1+n'^2)^2}-\frac{2\pi n'q^2}{(1+n'^2)}\right)\exp(q-2n'\cot^{-1}n'),$$

$$(12)\quad \oint\limits_{\xi} \frac{H(\xi)d\xi}{(1-2\iota k\xi)^3} = \left(\frac{4\pi n'^3(11n'^2-1)}{(1+n'^2)^3}+\frac{2\pi n' q^2}{(1+n'^2)}+\frac{16\pi n'^3 q}{(1+n'^2)^2}\right)\times$$
$$\times \exp(-q+2n'\cot^{-1}n')$$

Substituting these calculated values of the contour integrals the value of J splits up into two component parts —

$$\mathrm{J} = \exp(2n'\cot^{-1}n')\{\mathrm{K}\}+\exp(-2n'\cot^{-1}n')\{\mathrm{K}^*\},$$

where

$$\{\mathrm{K}\} = g_{-1}\frac{4\pi n'}{(1+n'^2)}+g_{-2}\frac{16\pi n'^3}{(1+n'^2)^2}+g_{-3}\frac{4\pi n'^3(11n'^2-1)}{(1+n'^2)^3}$$
$$+g'_{-1}\frac{4\pi n'\epsilon^{-q}}{(1+n'^2)}+g'_{-2}\left(\frac{16\pi n'^3\epsilon^{-q}}{(1+n'^2)^2}+\frac{4\pi n' q\epsilon^{-q}}{(1+n'^2)}\right)$$
$$+g'_{-3}\left(\frac{4\pi n'^3(11n'^2-1)\epsilon^{-q}}{(1+n'^2)^3}+\frac{16\pi n'^3 q\epsilon^{-q}}{(1+n'^2)^2}+\frac{2\pi n' q^2\epsilon^{-q}}{(1+n'^2)}\right),$$

$$\{\mathrm{K}^*\} = g_1\left(\frac{-4\pi n'}{(1+n'^2)}\right)+g_3\frac{4\pi n'^3}{(1+n'^2)^2}+g_1'\left(-\frac{4\pi n'\epsilon^{q}}{(1+n'^2)}\right)$$
$$+g_2'\frac{4\pi n' q\epsilon^{q}}{(1+n'^2)}+g_3'\left(\frac{4\pi n'^3\epsilon^{q}}{(1+n'^2)^2}-\frac{2\pi n' q^2\epsilon^{q}}{(1+n'^2)}\right)$$

The value of K is found to be zero after simplification, and that of K*

$$= \frac{4\pi n'\mathrm{G}_1(q)}{(1+n'^2)}+\frac{4\pi n'^3\mathrm{G}_2(q)}{(1+n'^2)^2},$$

where $\mathrm{G}_1(q) = (8/q^2+48/q^4)\cosh q-(24/q^3+48/q^5)\sinh q,$

$\mathrm{G}_2(q) = -32\cosh q/q^4+32\sinh q/q^5$

Hence the value of

$$\mathrm{J} = e^{-2n'\cot^{-1}n'}\left[\frac{4\pi n'}{(1+n'^2)}\mathrm{G}_1(q)+\frac{4\pi n'^3}{(1+n'^2)^2}\mathrm{G}_2(q)\right]$$

APPENDIX

TABLE IV

ν	Exp $\left[-2\pi\sqrt{\nu_0/(\nu-\nu_0)}\right]$	Cot^{-1} $\left[\sqrt{\nu_0/(\nu-\nu_0)}\right]$
$1\nu_0$	0 00000	0 0000
$2\nu_0$	0 00184	0 7854
$3\nu_0$	0 01180	0 9554
$4\nu_0$	0 02678	1 0475
$5\nu_0$	0 04328	1 1071
$6\nu_0$	0 06020	1 1504
$7\nu_0$	0 07330	1 1834
$8\nu_0$	0 09348	1 2094
$9\nu_0$	0 10861	1 2310
$10\nu_0$	0 13810	1 2490
$11\nu_0$	0 15260	1 2646

TABLE V

Values of $L = exp\left[-4\sqrt{\nu_0/(\nu-\nu_0)}\ \ cot^{-1}\sqrt{\nu_0/(\nu-\nu_0)}\right]$

(When $\nu = \nu_0$, $L = \epsilon^{-4} = 0\ 0183$)

$\nu = 2\nu_0$	L = 0 0433	$\nu = 7\nu_0$	L = 0 1449
$= 3\nu_0$	= 0 0670	$= 8\nu_0$	= 0 1601
$= 4\nu_0$	= 0 0890	$= 9\nu_0$	= 0 1753
$= 5\nu_0$	= 0 1093	$= 10\nu_0$	= 0 1892
$= 6\nu_0$	= 0 1278	$= 11\nu_0$	= 0 2021

TABLE VI

$X^2 = (2\ 514)\ (\nu_0/\nu)^2\ exp\ (-4n'\ cot^{-1} n')/(1-exp\ (-2\pi n'))$

(When $\nu = \nu_0$, $X^2 = 2\ 5140\,\epsilon^{-4} = 0\ 0461$)

$\nu = 2\nu_0$	X^2 = 0 0272	$\nu = 7\nu_0$	X^2 = 0 0080
$= 3\nu_0$	= 0 0189	$= 8\nu_0$	= 0 0069
$= 4\nu_0$	= 0 0143	$= 9\nu_0$	= 0 0060
$= 5\nu_0$	= 0 0114	$= 10\nu_0$	= 0 0055
$= 6\nu_0$	= 0 0095	$= 11\nu_0$	= 0 0051

TABLE VII

$F(X, S) = S^2/(1+S^2)(1+X^2-S)$ *

(When $\nu = \nu_0$, F(X, S) = 1 2330)

$\nu = 2\nu_0$	F(X, S) = 1 3150	$\nu = 7\nu_0$	F(X, S) = 1 4134
$= 3\nu_0$	= 1 3552	$= 8\nu_0$	= 1 4195
$= 4\nu_0$	= 1 3791	$= 9\nu_0$	= 1·4246
$= 5\nu_0$	= 1 3968	$= 10\nu_0$	= 1 4271
$= 6\nu_0$	= 1 4050	$= 11\nu_0$	= 1 4297

---

* We must remember that S has the value 0 7543 and S^2 the value 0 5619 when q has the value 1 418 in Hartree units.

TABLE VIII

$F^*(X, S) = S^2/(1-S^2)\ (1-X^2+S)$

(When $\nu = \nu_0$, $F^*(X, S) = 0{\cdot}7509$)

$\nu = 2\nu_0$	$F^*(X, S) = 0\ 7426$	$\nu = 7\nu_0$	$F^*(X, S) = 0\ 7344$
$= 3\nu_0$	$= 0\ 7390$	$= 8\nu_0$	$= 0\ 7339$
$= 4\nu_0$	$= 0\ 7370$	$= 9\nu_0$	$= 0\ 7335$
$= 5\nu_0$	$= 0\ 7358$	$= 10\nu_0$	$= 0\ 7333$
$= 6\nu_0$	$= 0\ 7350$	$= 11\nu_0$	$= 0\ 7332$

TABLE IX

$\Phi(\nu) = 0\ 7770(\nu_0/\nu) - 2\ 2038\ (\nu_0/\nu)^2$

ν	$\Phi(\nu)$	$[\Phi(\nu)]^2$
$1\nu_0$	−1 4268	2 035758
$2\nu_0$	−0 1624	0 026374
$3\nu_0$	0 0141	0 000199
$4\nu_0$	0 0565	0 003192
$5\nu_0$	0 0673	0 004529
$6\nu_0$	0 0683	0 004665
$7\nu_0$	0 0661	0 004369
$8\nu_0$	0 0627	0 003931
$9\nu_0$	0 0591	0 003493
$10\nu_0$	0 0557	0 003102
$11\nu_0$	0 0524	0 002746

Before proceeding to prepare a table for the absorption coefficient we should remember that according to our scheme of notation

$$\tau_\nu^+(e) = \frac{8\pi^3\nu e^2}{c}\, \mathrm{L}(\nu)F(\mathrm{X},\,\mathrm{S})\ \Phi^2(\nu)\,,$$

$$\tau_\nu^-(e) = \frac{8\pi^3\nu e^2}{c}\, \mathrm{L}(\nu)F^*(\mathrm{X},\,\mathrm{S})\ \Phi^2(\nu)\,,$$

and the values of the several factors have already been computed in the foregoing tables In the adjoining table X are attached the values of $\tau_\nu^+(e)$ and $\tau_\nu^-(e)$ when these are each divided by $8\pi^3\nu_0 e^2/c$

TABLE X

ν	$L(\nu)\Phi^2(\nu)$	$\overset{+}{\tau}_\nu(e)\Big/\frac{8\pi^3\nu_0e^2}{c}$	$\overset{-}{\tau}_\nu(e)\Big/\frac{8\pi^3\nu_0e^2}{c}$
$1\nu_0$	$3\ 7255\times10^{-2}$	$459\ 35\times10^{-4}$	$279\ 75\times10^{-4}$
$2\nu_0$	$0\ 1143\times10^{-2}$	$30\ 06\times10^{-4}$	$16\ 98\times10^{-4}$
$3\nu_0$	$0\ 0013\times10^{-2}$	$0\ 52\times10^{-4}$	$0\ 28\times10^{-4}$
$4\nu_0$	$0\ 0028\times10^{-2}$	$1\ 56\times10^{-4}$	$0\ 83\times10^{-4}$
$5\nu_0$	$0\ 0495\times10^{-2}$	$34\ 57\times10^{-4}$	$18\ 21\times10^{-4}$
$6\nu_0$	$0\ 0596\times10^{-2}$	$50\ 24\times10^{-4}$	$26\ 28\times10^{-4}$
$7\nu_0$	$0\ 0633\times10^{-2}$	$62\ 62\times10^{-4}$	$32\ 54\times10^{-4}$
$8\nu_0$	$0\ 0629\times10^{-2}$	$71\ 43\times10^{-4}$	$36\ 93\times10^{-4}$
$9\nu_0$	$0\ 0612\times10^{-2}$	$78\ 47\times10^{-4}$	$40\ 40\times10^{-4}$
$10\nu_0$	$0\ 0586\times10^{-2}$	$83\ 63\times10^{-4}$	$42\ 97\times10^{-4}$
$11\nu_0$	$0\ 0555\times10^{-2}$	$87\ 28\times10^{-4}$	$40\ 69\times10^{-4}$

TABLE XI

ν	$\Phi(\nu)$	$[\Phi(\nu)]^2$	$\overset{+}{\tau}_\nu\Big/\frac{8\pi^3\nu_0e^2}{c}L(\nu)F(X, S) = T(\nu) = \overset{-}{\tau}_\nu\Big/\frac{8\pi^3\nu_0e^2}{c}L(\nu)F^*(X, S)$	REMARKS
ν_0	$-1\ 4268$	$2\ 0358$	$6\ 2717\times10^{-2}$	Corresponding to the value of $M^v_{kk'}$ ($V''=0$, $V'=0$), viz, $3\ 0807\times10^{-2}$
$\nu_0+\frac{1}{4}\omega_0'$	$-1\ 4110$	$1\ 9909$	$6\ 1334\times10^{-2}$	
$\nu_0+\frac{1}{2}\omega_0'$	$1\ 3952$	$1\ 9466$	$5\ 9969\times10^{-2}$	
$\nu_0+\frac{3}{4}\omega_0'$	$1\ 3798$	$1\ 9038$	$5\ 8650\times10^{-2}$	
$\nu_0+\omega_0'$	$1\ 3640$	$1\ 8605$	$16\ 7858\times10^{-2}$	Corresponding to the value of $M^v_{kk'}$ ($V''=0$, $V'=1$), viz, $9{\cdot}0232\times10^{-2}$
$\nu_0+\frac{5}{4}\omega_0'$	$1\ 3496$	$1\ 8214$	$16\ 4330\times10^{-2}$	
$\nu_0+\frac{3}{2}\omega_0'$	$1\ 3349$	$1\ 7819$	$16\ 0767\times10^{-2}$	
$\nu_0+\frac{7}{4}\omega_0'$	$1\ 3203$	$1\ 7432$	$15\ 7275\times10^{-2}$	

ν	$\Phi(\nu)$	$[\Phi(\nu)]^2$	$\tau_\nu^{+} \Big/ \frac{8\pi^3\nu_0 e^2}{c} L(\nu)F(X, S) = T(\nu) = \tau_\nu^{-} \Big/ \frac{8\pi^3\nu_0 e^2}{c} L(\nu)F^*(X, S)$	REMARKS
$\nu_0+2\omega_0'$	1·3045	1 7017	$17\ 7120\times10^{-2}$	Corresponding to the value of $M_{kk'}^{v}$ $(V''=0,\ V'=2)$, viz, $10\ 4084\times10^{-2}$
$\nu_0+\frac{9}{4}\omega_0'$	1 2916	1 6682	$17\ 3133\times10^{-2}$	
$\nu_0+\frac{5}{2}\omega_0'$	1 2780	1 6333	$17\ 0000\times10^{-2}$	
$\nu_0+\frac{11}{4}\omega_0'$	1 2640	1 5977	$16\ 6295\times10^{-2}$	
$\nu_0+3\omega_0'$	1 2435	1 5588	$9\ 0883\times10^{-2}$	Corresponding to the value of $M_{kk'}^{v}$ $(V''=0,\ V'=3)$, viz, $5\ 8303\times10^{-2}$
$\nu_0+\frac{13}{4}\omega_0'$	1 2368	1 5297	$8\ 9186\times10^{-2}$	
$\nu_0+\frac{7}{2}\omega_0'$	1 2237	1 4974	$8\ 7303\times10^{-2}$	
$\nu_0+\frac{15}{4}\omega_0'$	1 2106	1 4656	$8\ 5449\times10^{-2}$	
$\nu_0+4\omega_0'$	1 1945	1 4268	$2\ 0141\times10^{-2}$	Corresponding to the value of $M_{kk'}^{v}$ $(V''=0,\ V'=4)$, viz, $1\ 4116\times10^{-2}$
$\nu_0+\frac{17}{4}\omega_0'$	1 1848	1 4038	$1\ 9816\times10^{-2}$	
$\nu_0+\frac{9}{2}\omega_0'$	1 1722	1 3741	$1\ 9397\times10^{-2}$	
$\nu_0+\frac{19}{4}\omega_0'$	1 1597	1 3449	$1\ 8985\times10^{-2}$	
$\nu_0+5\omega_0'$	1 1448	1 3106	$0\ 0709\times10^{-2}$	$M_{kk'}^{v}$ $(V''=0,\ V'=5) = 0\ 0541\times10^{-2}$
$\nu_0+6\omega_0'$	1 0960	1 2012	$0\ 0400\times10^{-2}$	$M_{kk'}^{v}$ $(V''=0,\ V'=6) = 0\ 0333\times10^{-2}$

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STRUCTURE AND DEVELOPMENT OF THE OVULE AND EMBRYO SAC OF *LASIOSIPHON ERIOCEPHALUS* DCNE

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(Communicated by Prof A C Joshi, D Sc)

(*Received January 31, 1940*)

INTRODUCTION

The earliest embryological investigation on the Thymelaeaceae is by Hofmeister in 1849 on *Daphne* and since then a number of contributions have appeared from time to time Schnarf (1931) has reviewed these in his treatise on the angiosperms and has given the following summary of the embryology of the family

The development of pollen follows the simultaneous type In *Daphne* a transitory cell plate is formed during the heterotypic division The mature pollen contains three nuclei The ovule has a massive nucellus with two integuments According to Guérin (1913, 1915) there is a remarkable development of the nucellar vascular bundle in a few members of the Thymelaeaceae, namely, *Dicranolepis*, *Craterosiphon* and *Synaptolepis* The archesporium consists of a single cell which divides to give rise to a parietal cell and the megaspore mother cell The development of the embryo sac follows the normal type The antipodals are variable, they are small in *Wickstroemia indica*, *W canascens*, *Gnidia carinata* and *Daphne alpina*, but show an increase in number in *Daphne odora* (three to six), *Blagayana pseudomezereum*, *Thymelaea passerina*, *Dirca palustris* (numerous) and *Daphnopsis Schwartzii* (many or three) In most species an obturator develops at the base of the stylar canal for the conduction of the pollen tubes towards the micropyle The endosperm is free nuclear Abnormalities occur in the family the phenomenon of sterility in *Daphne odora* (Osawa, 1913) and somatic parthenogenesis and associated nucellar embryony in *Wickstroemia indica*

Since the publication of Schnarf's work some further investigations have been made recently Joshi (1937) has studied the development of the pollen in *Thymelaea arvensis*, *Wickstroemia indica* and *Daphne Mezereum* Fuchs (1938) has made a detailed study of the embryology of some members of the family and has also discussed the affinities

The present paper is based on a morphological and embryological study of *Lasiosiphon eriocephalus* Dcne with particular reference to some important features in the development of the embryo sac and in the structure of the ovule.

VOL. VI—No. 1. Published June 15th, 1940.

MATERIAL AND METHODS

The material for investigation was collected from the forests of the Western Ghats in the Mysore State during the month of December, 1938 Bouin's fluid was largely used for fixation In addition, material preserved in formalin-acetic acid-alcohol was also made use of The regular methods of dehydration and infiltration were followed In some cases the material was run through mixtures of alcohol and chloroform and infiltrated in pure chloroform By this method many of the difficulties in sectioning the material, especially in old stages when the floral parts become hard, were overcome to a certain extent All the sections were stained in Heidenhain's iron-alum haematoxylin which was quite satisfactory

THE FLOWER

The flowers are grouped together in dense head-like inflorescences and develop according to a racemose plan Each flower has a single whorl of perianth which forms a long tube (fig 3), at the top of which are seen five small imbricating segments of the perianth The outer surface of the perianth is densely clothed over by numerous silky hairs In very advanced stages of the flower the upper half of the perianth becomes detached by the formation of an abscission layer and the lower half remains as a loose membranous covering for the developing fruit

There are ten stamens in two alternating whorls of five each and these are adnate to the perianth The vascular connections to the outer (upper) whorl of stamens are separated from the midrib bundles of the perianth, while those to the inner (lower) whorl are separated from the combined lateral strands supplying the adjacent margins of the perianth segments Outside the outer whorl of stamens and alternating with these and the perianth segments there are five fleshy parenchymatous scale-like structures which are roughly bifid (fig 4) These do not have any vascular connections and may, therefore, be regarded merely as lobes formed by the perianth segments

The ovary is raised on a short stalk and contains a single ovule The style is long and narrow and terminates in a head-like stigma (fig 5) The peripheral epidermal cells of the stigma become conspicuous very early with rich contents and gradually form a number of papillae (figs 6, 7) These papillae next become elongated considerably to form short hairs (fig 8) amidst which the pollen grains are deposited After the receptive function is over the stigmatic hairs are filled with tannin and later may either persist as such or may drop off

The external surface of the ovary is covered over by hairs similar to those found on the perianth These hairs gradually fall off later as the fruit begins to be formed

At the base of the ovary a conspicuous ring-like disc-scale develops. This is provided with vascular connections from the receptacular stele (fig 3)

This disc-scale is regarded as a much reduced inner whorl of floral leaves, the corolla, as suggested by Joshi (1936) in another member of the Thymelaeaceae, *Stellera chamæjasme*

DEVELOPMENT OF THE MICROSPORANGIUM

The primordia for the two sets of stamens are formed very early in the ontogeny of the flower They are at first made up of uniform cells without any differentiation As further growth takes place, a single layer of cells becomes clearly marked out within the epidermis (fig 10) This layer constitutes the archesporium of the anther which next divides periclinally to form an outer primary parietal layer and an inner sporogenous layer The former divides again periclinally immediately to form two layers (fig 11), of which the outer without further divisions functions as the endothecium in the mature anther, while the inner divides for the last time periclinally to give rise to the single middle layer and the tapetum (fig 12) The tapetum lies in immediate contact with the sporogenous layer, the cells of which have divided in the meanwhile to form two layers of microspore mother cells

During the development and increase in the size of the tapetal cells and the spore mother cells, both the endothecium and the single middle layer are greatly crushed tangentially (fig 13) With the increase in the size of the tapetal cells, which marks the commencement of their activity, the nucleus of each cell divides once mitotically so that the tapetal cells finally become binucleate At this time the cells are more or less bulging with their inner walls rounded off (fig 13)

Just as a tapetal layer is formed towards the outside of the sporogenous cells, it is also formed towards the inside by the cells of the connective tissue of the anther These inner tapetal cells are exactly similar to the outer ones both in shape, as well as in contents, being also similarly binucleate (fig 13) In the older stages of the anther, the tapetal cells break down and their disorganised remnants may be seen as darkly staining scattered bits within the wall of the anther

DEVELOPMENT OF THE MEGASPORANGIUM AND THE FEMALE GAMETOPHYTE

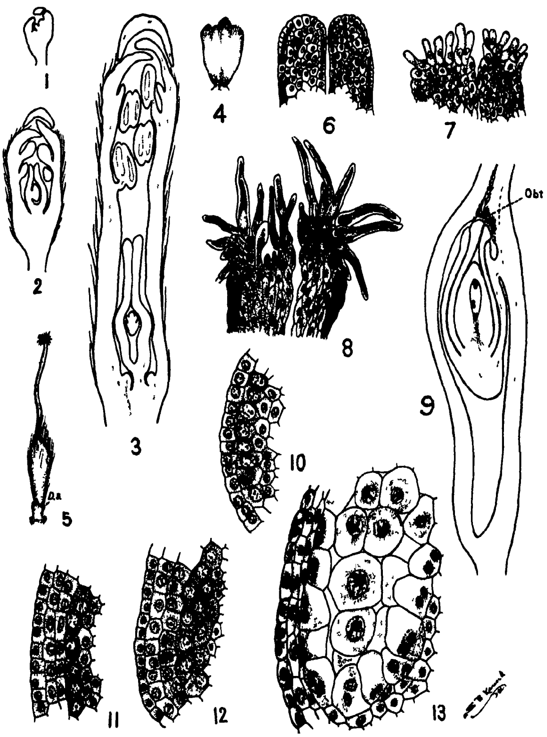
As already stated, the ovary contains a single ovule which is attached laterally on the placenta with the micropyle pointing upwards (fig 9) The ovule first develops as a mass of undifferentiated tissue and gradually assumes its typical structure by forming two annular rings of tissue one below the other (figs 3, 15) These are the primordia of the two integuments At this stage a large space is seen developing in the cavity of the ovary below the ovule (fig 3) This space persists characteristically in subsequent stages and although an attempt was made to verify if this represented any provision for the development of a second ovule, no evidence for this was forthcoming. In later stages, when the seed begins to develop after fertilisation, the space is partly filled up by the downward growth of the base of the seed, while a small portion of it still remains and becomes filled with air

During the development of the ovule, the micropyle comes in contact with a special tissue formed at the base of the stylar canal (fig 9) This tissue consists of regularly arranged elongated cells containing abundant material and projecting into the ovarian cavity (fig 14) This is the obturator which functions as a device for the conduction and growth of the pollen tubes as they descend from the stylar canal towards the micropyle The obturator is characteristic of most of the Thymelaeaceae and it is also met with in certain other families, as Euphorbiaceae, Rosaceae, Elaeagnaceae, Umbelliferae, etc The morphology of the obturator, however, is different in the several cases, for it arises either from the placenta or the funiculus, while in the Thymelaeaceae it is a specialised part of the transmitting tissue which fills the stylar canal

After the inception of the integument primordia, both the integuments, which in most subsequent stages of development are free from each other, grow at first uniformly all round the nucellus (fig 16) But after a time the inner integument grows more rapidly than the outer and alone forms the micropyle (fig 9) The upper part of the inner integument at the region of the micropyle becomes conspicuous as a conical projection surmounted by a knob formed by the flaring rim of the integument (fig 9) The rim of the outer integument stops short behind the knob and invests the part below the knob as a tight-fitting collar Later, however, as the seed develops the outer free portion of the rim of the outer integument, namely that lying on the opposite side of the placenta, grows beyond the knob and, closely arching over, forms a hood-like covering for the micropyle (fig 20)

Both the integuments are at first made up of three layers of cells except at the base where there may be four layers (fig 15) Gradually the number of cell layers in the inner integument increases to four, and the cells, filled with dense cytoplasm, show a very regular arrangement (fig 21) In the meanwhile the outer integument forms five layers of regularly arranged cells, which are not only larger than those of the inner integument, but also contain less cytoplasm and include vacuoles (fig 21) As further growth of the ovule proceeds, the inner integument also becomes five layered, but all the cells, except those forming the inner epidermis, now contain only a little cytoplasm and extremely reduced nuclei (fig 21). This evidently means that the materials once stored in the cells of the inner integument have passed into the nucellus for its growth At this time the cells of the outer epidermis of the inner integument become radially elongated, and still later, when the seed develops, appear as a palisade layer made up of columnar cells (fig 23) This feature is especially marked at the base of the integument

Simultaneous with the changes in the inner integument as described above, the outer integument also shows further transformations The number of cell layers remains as before, namely five, but the cells lose their regular



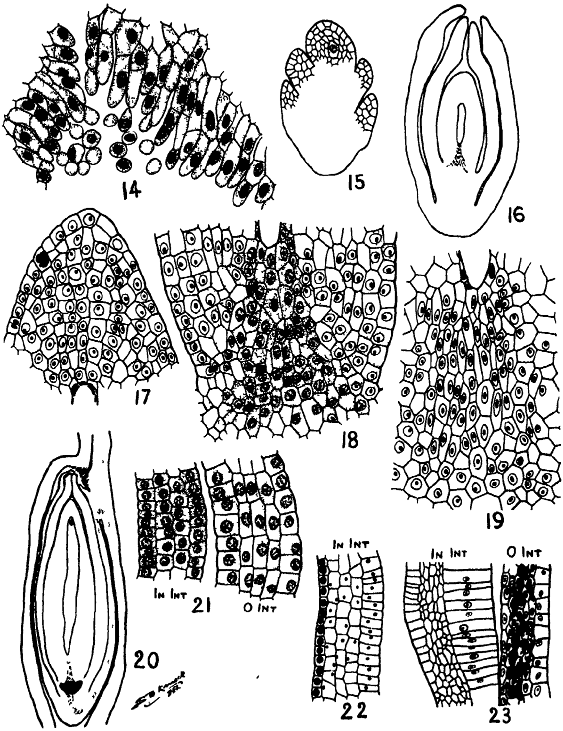
FIGS 1–13 Figs 1–3 Stages in the development of the flower ×40 Fig. 4. Scale like lobe of the perianth Fig 5 Entire ovary showing disc-scale, *D.S.* ×6 Figs 6-7 The stigmatic hairs forming as papillae ×200 Fig. 8. Same, later stage showing tannin in the hairs ×120 Fig. 9 Longitudinal section of ovary showing the position of the ovule and the obturator ×40 Figs 10–13 Stages in the development of the anther wall ×450

arrangement Further, the cells of the inner layer become tannin-filled and take a brownish stain with haematoxylin (fig 23) In the developing seed, the outer integument becomes very much compressed and forms a thin but fibrous covering for the seed

After the formation of the primordia of the integuments the inner mass of tissue, the nucellus, begins to grow rapidly The apex of the nucellus assumes a more or less conical shape and the epidermal cells of this region begin to undergo a series of periclinal divisions to form the so-called epidermal cap (fig 17) Below this cap a large amount of tissue with rich contents is recognisable This tissue is designated by Fuchs (1938) as the 'Deckzollenkomplex' and is derived by the divisions of the primary parietal cell formed by the archesporium This tissue, together with the overlying epidermal cap, gives a somewhat glandular appearance to the apex of the nucellus (*cf* Proteaceae, Brough, 1933, Kausik, 1938*a*, 1938*b*, 1939), and is perhaps of advantage in the passage of the pollen tubes towards the embryo sac which is situated far below The cells of the nucellus below the apex are also fairly well filled with materials although not to the same extent But at the base of the nucellus and immediately below the antipodal end of the embryo sac a region of extremely rich cells develops conspicuously which are elongated and regularly arranged to form a strand of tissue (figs 18, 19) This strand functions as a conducting strand for supplying materials to the embryo sac for its growth, not only prior to fertilisation, but also afterwards when the embryo sac elongates remarkably The conducting strand spreads out at the base of the nucellus like a pedestal surmounted by the embryo sac

Fuchs (1938) describes the presence of a conducting strand in her study of the other members of the Thymelaeaceae It is also met with in the Lythraceae (Joshi and Venkateswaralu, 1936) and in the Geissolomataceae (Stephens, 1909*a*) In the latter instance it appears to offer a certain amount of obstruction to the antipodal end of the embryo sac during its post-fertilisation elongation and is left over as a bundle of tissue projecting into the embryo sac when the latter grows down and all round it Kershaw (1909) states that a conducting strand is present in the ovule of ***Myrica Gale*** and remarks that it may either represent the remains of an ancient nucellar vascular system or that it may be an entirely new structure developing at the base of the nucellus In the Thymelaeaceae Guérin (1913, 1915) has found the nucellar tracheal tissue in some members, but it is absent in the other members studied by Fuchs (1938) and also in ***Lasiosiphon*** It may, therefore, be suggested that the conducting strand, which is characteristic of the Thymelaeaceae and is also met with in other families which may not be related to one another on other grounds, may be regarded as a special device formed at the base of the nucellus and in response to the nutritive demands made by the embryo sac

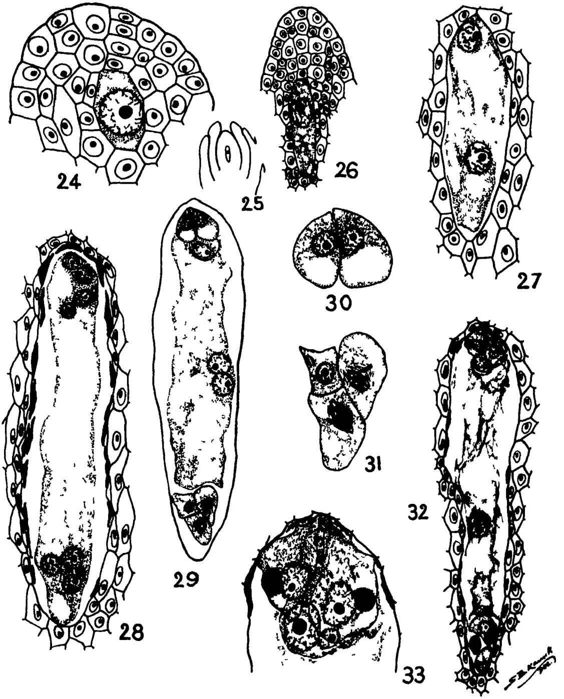
The female gametophyte —It is hard to detect the presence of the archesporial cell in the nucellus of the young ovule as all the cells are similar But in slightly older ovules, when the integuments have just been formed, there is



FIGS 14–23 Fig 14 Base of the stylar canal showing the obturator. × 400 Fig 15 Young ovule showing the megaspore mother cell and the origin of the integuments. × 200 Fig. 16 Same, later stage showing the conducting strand at the base of the nucellus × 200 Fig 17. Apex of the nucellus showing formation of epidermal cap and the massive parietal tissue × 400. Figs 18, 19 Base of nucellus showing conducting strand. × 400. Fig. 20. Longitudinal section of seed with hypostase marked black. × 20. Fig 21. Part of the integuments to show details. × 400. Fig 22. Part of inner integument later. × 200. Fig. 23 Part of both integuments from the seed. × 200.

already seen a single large cell which by its position and characteristics must be regarded as the megaspore mother cell (figs 15, 24) Overlying this there are two cells which are evidently formed from the parietal cell which has divided once periclinally soon after its formation from the archesporial cell (fig 24) At this stage some of the epidermal cells at the apex of the nucellus have divided to form the epidermal cap so that the megaspore mother cell lies four cells below the outer surface of the nucellus The mother cell next elongates rapidly (fig 26) before undergoing the two divisions in the formation of the linear tetrad The actual stages leading to the development of the tetrad and the survival of one megaspore to form the embryo sac were not available A considerable time seems to elapse before any activity sets in in the mother cell during which it undergoes a period of rest The next stage available in development was one shown in fig 27 where the two nuclei of the young embryo sac are already formed and these have taken up their respective positions at the two ends At this stage some vacuoles are seen in the embryo sac and attention may be specially drawn to one such vacuole below the primary chalazal nucleus This vacuole persists in later stages and is present even after all the eight nuclei are formed (fig 28) It is interesting to note here that a chalazal vacuole has been figured by Mauritzon (1934) at the two-nucleate stage of the embryo sac in *Cuphea lanceolata* and *C platycentra* and by Joshi and Venkateswaralu (1936) in some of the other members of the Lythraceae The latter authors state that 'the binucleate embryo-sac, as in *Lagerstroemia*, is often characterised by the persistence of the chalazal vacuole for an unusually long period and sometimes this condition is seen even during the development of the 4-nucleate embryo-sac or after its formation' They further remark that this feature and the early degeneration of the antipodals in the Lythraceae, besides a few other minor ones, 'have been regarded by Tischler (1917) and Mauritzon (1934) to indicate that the embryo-sac of the Lythraceae forms phylogenetically an intermediate stage between the 4-nucleate embryo-sac of the Onagraceae and the normal 8-nucleate embryo-sac' On the same ground it is reasonable to postulate here on the probable relationship of the Thymelaeaceae with the Lythraceae, between which families there also appear to be other almost parallel structural features in the development of the ovule In fact there is some justification for this, for according to Hutchinson (1926) the Thymelaeales are to be regarded as the 'increasingly woody apetalous relations of the Lythrales'

After the establishment of the eight nuclei the organisation of the embryo sac begins with the formation of the egg-apparatus, the antipodal cells and the two polar nuclei (fig 29) The cytoplasm of the embryo sac is highly vacuolate and becomes more so a little later The synergids are at first roughly pear-shaped with a large basal vacuole and a dense mass of cytoplasm containing the nucleus at the apex (figs 29, 30) As the embryo sac reaches the stage of fertilisation, the synergids show each a slight beak-like projection appearing as a hump on the free outer side (figs 32, 33) The nucleus assumes a more



FIGS. 24–33 Fig. 24 Part of nucellus with megaspore mother cell with formation of epidermal cap and two parietal cells ×900 Fig 25 Ovule with megaspore mother cell later ×80 Fig 26 Part of same enlarged ×450 Figs. 27, 28 Two and eight nucleate embryo sacs respectively with chalazal vacuole ×900 Fig 29 Fully formed embryo sac ×400 Figs 30, 31 The synergids and the antipodals from the same enlarged and showing division of nucleus in two antipodals ×900 Fig 32 Embryo sac at the time of fertilisation and triple fusion ×450 Fig. 33 Micropylar end of same enlarged to show a male nucleus in contact with the egg nucleus and the special spherical body in each synergid, both synergids are intact and the pollen tube has entered behind and between these ×1350.

or less central position, and in contact with this there is sometimes seen a dense spherical body stained brownish with haematoxylin in each synergid (fig 33) It is rather hard to discuss the nature of this extra body, but the suggestion that it may probably represent some special substance stored up in the synergid to facilitate the entry of the pollen tube by its chemotactic influence does not seem to be wholly unwarranted This suggestion is further strengthened by the fact that in such cases both the synergids are often left intact when the pollen tube enters the embryo sac and discharges its contents (fig 33) The further fate of this body could not be studied and it is sufficient to mention that it disappears from view in later stages when the synergids begin to degenerate some time after fertilisation

It may be mentioned here that the body mentioned in the synergids looks very much like the kinoplasmic mass seen in the egg cell of some gymnosperms Land (1904) describes in the case of *Ephedra trifurca* that 'a conspicuous kinoplasmic mass lies at a little distance below the nucleus' of the central cell of the archegonium He further remarks 'In the earliest stages it is coarsely granular, and later becomes dense, and is larger and sharper in outline than the similar body which is so conspicuous in some of the pines and in *Thuja occidentalis*'

The antipodals are three in number, but in some cases the nucleus in each cell divides once mitotically (figs 29, 31), followed by the separation into daughter cells Either all the antipodals take part in this division, or only one or two may divide, so that finally the number of antipodals in a mature embryo sac varies from three to six After fertilisation all these cells begin to degenerate and in later stages are recognisable only as heavily stained specks at the lower end of the embryo sac

The two polar nuclei meet each other at first in the centre of the embryo sac (fig 29), but may subsequently be found anywhere in the lower end or even very near the antipodals Their union is considerably delayed and seems to take place regularly just prior to triple fusion The two polar nuclei in a half fused state, showing distinctly two independent chromatin masses and two nucleoli, were seen with the second male nucleus closely perched on them as shown in fig 32 Fuchs (1938) remarks that the two polar nuclei wander towards the chalazal end and states that she could not observe their fusion in her materials

During all the stages leading to the final organisation of the embryo sac the neighbouring cells of the nucellus are crushed to a large extent and appear as several scattered bits all round the embryo sac Thus these cells not only afford extra space for the enlarging embryo sac but also supply it with materials that are stored up in the earlier stages

FERTILISATION

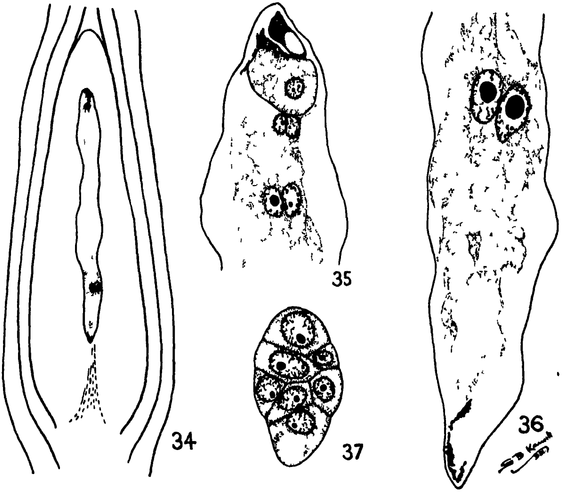
Stages showing the actual entry of the pollen tube into the embryo sac were not seen in any of the preparations But slightly advanced stages with the discharged pollen tube were met with In such cases one of the two synergids was intact, while the other had been destroyed by the pollen tube The surviving synergid was seen persisting even in later stages when the embryo sac had formed a few free endosperm nuclei (fig 35) Sometimes both the synergids were found to be quite intact even though the pollen tube had entered and the two male nuclei were in association with the egg nucleus and the polar nuclei (fig 32) It was in such a case that the spherical body already referred to was noticed in the synergids and as suggested it is probable that it has a definite rôle to perform in the actual entry of the pollen tube passing between and behind the synergids as shown in fig 33 In this figure, the disorganised remnants of the tip of the tube are clearly seen as a number of dark specks scattered in the vicinity of the egg-apparatus and marking the track of the pollen tube Joshi and Kajale (1937) have shown that both the synergids are frequently intact during fertilisation in *Alternanthera sessilis* and in earlier literature such a condition has also been noted in *Salix* (Chamberlain 1897) and *Silphium* (Merrell, 1900)

Fertilisation and triple fusion occur regularly in *Lasiosiphon eriocephalus* The first male nucleus fuses with the egg nucleus, while the second travels down the embryo sac rapidly and fuses with the two polar nuclei which are uniting with each other just now The actual fusion of the male nuclei seems to be simultaneous in both fertilisation and triple fusion

DEVELOPMENT OF THE EMBRYO AND ENDOSPERM

The first division in the fertilised egg takes place only after a few free endosperm nuclei are formed This division takes place by a transverse wall to form a proximal or basal cell and a distal cell The second division, presumably also by a transverse wall, is formed in the distal cell so that the pro-embryo becomes three-celled as noted by Fuchs (1938) The further divisions are irregular and take place by inclining and interesting walls to form an oval embryo in which the distal and the proximal ends are clearly seen There is a basal cell with large vacuoles (fig 37) As further growth in the embryo proceeds the histogens are formed after which the embryo grows rapidly, encroaches on the endosperm and occupies the entire cavity of the seed in the mature condition

The endosperm first arises in a free nuclear state and very early in development shows a paired arrangement of these nuclei at the micropylar, central, and chalazal portions of the embryo sac (figs 34, 36) The pair of nuclei at the chalazal end is particularly conspicuous by their large size, and being embedded in a dense mass of cytoplasm (fig 36) appears to take part to a considerable degree in the absorptive activity of the lower end of the embryo sac Fuchs (1938) states that in later stages, when the endosperm becomes cellular, the lower end of the embryo sac contains large cells which have either many nuclei each or a single giant nucleus The two large nuclei noted in the present case probably give rise by further divisions to the giant nuclei described by her



Figs 34–37 Fig 34 Part of longitudinal section of seed to show a few free endosperm nuclei ×40 Figs 35, 36 Micropylar and chalazal ends to show the fertilised egg, one of the surviving synergids, and the paired arrangement of endosperm nuclei, the chalazal pair of nuclei is prominently seen in fig 36 ×900 Fig 37 A small many-celled embryo with rounded distal and wedge-shaped proximal ends. ×900

After a large number of free nuclei are formed in the embryo sac, the endosperm tissue is built up which includes large and irregular cells This tissue is rapidly encroached upon later by the growing embryo and is completely destroyed by it when the seed reaches the mature condition

THE SEED

The seed has a hard seed-coat formed by the two integuments The outer integument forms a fibrous covering which may be easily peeled off from the seed, while the inner remains as a very rigid and firm investment for the embryo The outer epidermis of this integument forms a woody palisade layer (fig 23) as mentioned by Fuchs (1938) The base of the seed shows a thick pad of tannin-filled tissue, the *hypostase*, which takes up a very heavy stain (fig 20) Within the seed-coat, a thin layer of nucellus persists all around as a lining for the embryo, while the apex of the nucellus projects conically into the narrow micropyle

CONCLUSIONS

The present account of the embryology of *Lasiosiphon eriocephalus* Dcne conforms in all respects to the earlier investigations in the family and includes a detailed study of some important features in the development of the ovule and the embryo sac The noteworthy points in the life-history are the presence of the obturator, the formation of the epidermal cap and the cell complex arising from the parietal tissue in the ovule, and the presence of a conducting strand at the base of the nucellus In the development of the embryo sac the presence of the chalazal vacuole has been pointed out and it has been suggested that in this feature, as well as in a few others, evidence for kinship between this family and the Lythraceae may be forthcoming The presence of a special body in the synergids, which appears to be recorded here for the first time, can only be interpreted as a special feature of the synergids to help in the entry of the pollen tube into the embryo sac and its association in cases where both the synergids are left intact at the time of fertilisation lends additional support to this surmise

The development of an oval embryo without a suspensor seems to resemble the condition in *Geissoloma marginata* (Stephens, 1909*a*) belonging to the Geissolomataceae and also found in the Penaeaceae (Stephens, 1909*b*) In the family Proteaceae also, which is regarded by some to be related to the Thymelaeaceae, it is curious to find a spherical (according to Ballantine, 1909 and Brough, 1933), but more correctly an oval, embryo (Kausik, 1938*a*, 1939) This fact, along with the presence of the glandular apex of the nucellus formed by the parietal tissue in both the Thymelaeaceae and the Proteaceae, appears to offer some ground for considering the relationship between the two families as really valid From the point of floral anatomy also additional light seems to be thrown on this question, for in both the families the perianth represents the whorl of calyx (Joshi on *Stellera*, 1936, Kausik on *Macadamia*, 1938*b*, 1940), while the corolla is very much reduced and is represented by the disc at the base of the ovary Thus the ancestral condition in both has to be regarded as a dichlamydeous one and the modern members have become simple through reduction The arrangement of Bentham and Hooker (1862–1883) to include both these families under the Monochlamydeae must, therefore, be considered as unjustified

Fuchs (1938) has discussed the systematic position of the family from an embryological standpoint and states that it is surprising that there are such great differences between the closely related families Penaeaceae, Geissolomataceae and the Thymelaeaceae It may be remarked here that these embryological differences may only mean individual specialisations in these several families and may not be fundamental in settling the affinities of these families In the case of the Penaeaceae (Stephens, 1909*b*) it is true that there is the development of a 16-nucleate embryo sac by the participation of all the four megaspores, but Stephens suggests that it is a derived condition from, perhaps, the Geissolomataceae (1909*a*) which shows a normal development Fuchs (1938) further discusses the systematic position of the Thymelaeaceae with the other families of the Myrtiflorae according to Engler and Gilg (1924) and states that in the possession of an obturator the family stands sharply distinct from all the others and points out that only the Elaeagnaceae, where a sort of an obturator is formed, come very close to the Thymelaeaceae

Joshi (1938) has considered the affinities of the Thymelaeaceae from floral anatomy and points out from a study of *Stellera chamaejasme* that the arrangement of Hutchinson (1926) to include the family Nyctaginaceae also in the order Thymelaeales cannot be justified He further states that the Thymelaeaceae must have come from dichlamydeous ancestors as the disc-scale represents a much reduced inner whorl of floral leaves, the corolla The present writer is in complete agreement with this view Joshi also proposes that the two subfamilies, the Aquilarieae and the Thymeleae, may be brought closer together on account of anatomical evidence for a bicarpellary gynoecium in *Stellera* belonging to the Thymeleae, which is generally regarded as possessing a monocarpellary gynoecium Fuchs (1938) states that while the gynoecium in the family is usually made up of a single carpel, the Aquilarioideae and the Phalerioideae possess two carpels, while *Octolepis* has four It, therefore, seems quite tenable that a reduction in the number of carpels has taken place in the family and that ancestrally there were more carpels As an extensive study of the floral anatomy of *Lasiosiphon* does not fall within the scope of the present investigation, a more detailed approach to this question cannot now be made.

SUMMARY

1 The structure of the flower and the development of the anther and the ovule are described in detail

2 The wall of the anther has four layers the epidermis, endothecium, a single middle layer, and the tapetum All these layers except the epidermis are formed from the primary parietal layer The tapetal cells become binucleate and similar cells are also formed by the cells of the connective tissue of the anther towards the sporogenous layer

3 In the developing ovule the apex of the nucellus becomes conspicuous with the formation of the epidermal cap and the cell complex arising from the primary parietal cell There is a conducting strand at the base of the nucellus for supplying nutrition to the growing embryo sac

4 The megaspore mother cell is formed by the archesporial cell after a parietal cell is cut off The further behaviour of the mother cell is normal and the embryo sac develops according to the usual type

5 A chalazal vacuole is seen in the developing embryo sac even after the 1-nucleate stage and its significance is considered in the light of previous literature

6 The synergids sometimes show a spherical body which is regarded as a special substance to aid in the entry of the pollen tube into the embryo sac Both the synergids are then found intact when the pollen tube enters, while at other times when the body is not seen one of the two synergids degenerates as usual

7 The first division of the fertilised egg takes place only after a few free endosperm nuclei are formed The embryo becomes oval in form during development and lacks a suspensor

8 The endosperm is at first free nuclear and later forms a loose tissue made up of large and irregular cells During the free nuclear condition two large nuclei are found at the chalazal end and they are probably concerned actively in the haustorial function of the lower end of the embryo sac

9 As the seed develops the endosperm tissue is completely used up by the embryo The structure of the mature seed is described in the paper

10 The affinities of the Thymelaeaceae are considered, and it has been pointed out that, as Joshi (1936) suggests, the family is derived from dichlamydeous ancestors

ACKNOWLEDGMENTS

In conclusion I have pleasure in recording my sincere thanks to Dr A C Joshi, of the Benares Hindu University, for many courtesies and for his kind help in the publication of this paper Further, I am grateful to Prof M A Sampathkumaran, Head of the Department of Botany, University of Mysore, for much encouragement during the course of this work. Finally, I wish to express my appreciation of the help rendered by Mr D Srinivasachar, M Sc, now at the Imperial Agricultural Research Institute, New Delhi, in kindly collecting the material at my request

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Thirteenth Ordinary General Meeting.

The Thirteenth Ordinary General Meeting of the National Institute of Sciences of India was held in the University Chemical Laboratories, Lahore, on the 11th and 12th March, 1940 Owing to the absence of the President and the Vice-Presidents, Khan Bahadur M Afzal Husain was appointed chairman

Present Khan Bahadur M Afzal Husain
Prof S S Bhatnagar
Dr H Chaudhuri
Principal B L Bhatia
Prof S L Ghose
Prof P K Kichlu
Mr E S Pinfold
Prof J N Ray
Prof S P Agharkar, *Honorary Secretary*

Besides the Fellows there were also present about 80 visitors on the 11th and 110 visitors on the 12th March, 1940

1 The minutes of the 5th Annual General Meeting held on the 2nd January, 1940, were read and confirmed

2 The following Fellow signed the duplicate obligation and was admitted as a Fellow under Rule 13

Prof P K Kichlu

3 The following papers were taken as read owing to the absence of the authors —

(1) On the structure of atomic nuclei By M N Saha, S C Sircar and K C Mukherji

(2) On the theory of spiral nebula By D N Moghe (communicated by Principal G S Mahajani)

(3) On the theory of a system of receding particles having a tendency to approach the central mass By D N Moghe (communicated by Principal G S Mahajani)

(4) The second maximum of the Rossi curve By N N Das-Gupta (communicated by Prof M N Saha)

(5) The continuous spectrum of hydrogen excited by canal rays of hydrogen By V T Chiplonkar (communicated by Prof M N Saha)

4 The following papers were read —

(1) On the constitution of *Chokshin*, a new drug—from Cassia abrus By Kartar Singh Narang, J N Ray and K N Gaind

(2) Magnetochemical methods in chemical research By P L Kapur and S S Bhatnagar

5 At the adjourned meeting on the 12th March, 1940, a Symposium was held on 'Some aspects of the application of Science to the development of Indian Industries'

The following papers were read —

(1) Geology and the search for oils By E S Pinfold
(2) The drug industry in India By J N Ray
(3) Defence Co-ordination and National Planning By Lala Feroz Chand
(4) Petroleum Products and National Economy By F J Ward
(5) National Planning By Ruchi Ram Sahni.

The papers will be published in due course in the *Proceedings* of the National Institute of Sciences of India

With a vote of thanks to the chair the meeting terminated

Prof S S Bhatnagar entertained Fellows of the National Institute to lunch on the 11th and Khan Bahadur M Afzal Husain to tea on the 12th March, 1940

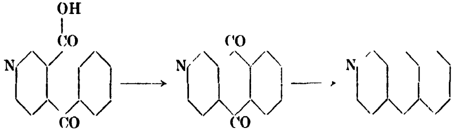
STUDIES IN THE ISOQUINOLINE SERIES *

PART IV SYNTHESES OF BENZO-ISOQUINOLINES AND A STUDY OF THE METHODS OF PREPARING ISOQUINOLINES FROM THE NAPHTHALENE RING

By B B DEY *and* S RAJAGOPALAN

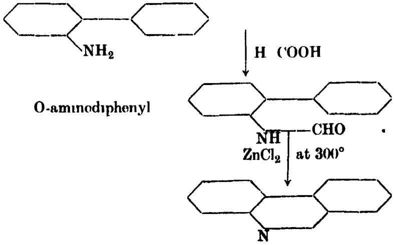
(*Read January 2, 1940*)

The first synthesis of a benzo-isoquinoline (6 7) appears to have been carried out by Phillips (*Ber*, 1894, *27*, 1923 1895, *28*, 1658), who proceeded in an indirect way, according to the following scheme —



6 7-benzo-isoquinoline

A different method was adopted by Pictet and Hubert (*Ber*, 1896, *29*, 1183), who prepared 3 4-benzo-isoquinoline and a few substituted products, albeit in poor yields, in the following way —



O-aminodiphenyl

3 4-benzo-isoquinoline.

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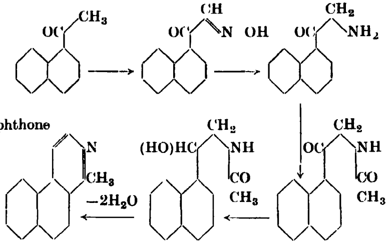
* Parts I–III appeared in the *Archiv der Pharmazie, Berlin*, 1937, pp 383–397, pp 397–405; and 1939, pp 177–192

VOL. VI—No. 2. [Published July 19th, 1940.

Later, Pictet and Manevitch (*Arch Sci. Phys Nat*, 1913, *35*, 40) claimed to have effected the direct syntheses of 1-methyl-5 6-benzo-isoquinoline with a naphthalene compound as the starting material, by the steps indicated below —



α-acetonaphthone

1-methyl-5 6-benzo-isoquinoline

We have carefully repeated this work, but we have been unable, in spite of repeated attempts, to carry out the last stage, i e cyclisation of the amide to the isoquinoline

The next syntheses of compounds of this class were those of 1-methyl-3 4-dihydro-5 6-benzo-isoquinoline and 1-methyl-3 4-dihydro-7 8-benzo-isoquinoline, accomplished by Gibson, Hariharan, Menon and Simonsen (*J Chem Soc*, 1926, 2247) They started from α- and β-naphthaldehydes and proceeded in the following stages —

$$C_{10}H_7\ CHO + (CH_3)_2\ CO$$

$$\downarrow$$

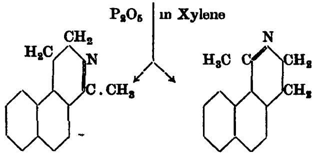
$$C_{10}H_7\ CH\ CH\ CO\ CH_3$$

$$\downarrow H_2$$

$$C_{10}H_7\ CH_2\ CH_2\ CO\ CH_3$$

$$\downarrow NH_2\ OH$$

$$C_{10}H_7\ CH_2\ CH_2\ C\ (N\ OH)\ CH_3$$

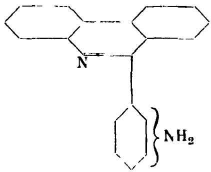


1-methyl-3 4-dihydro-5 6-benzo-isoquinoline

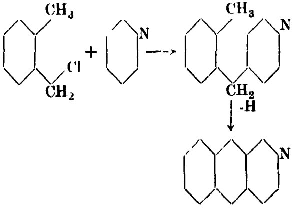
1-methyl-3 4-dihydro-7. 8-benzo-isoquinoline.

The yields were stated to be exceedingly poor

Lately, Morgan and Walls (*J Chem Soc*, 1931, 2447) successfully applied the Bischler-Napieralsky method to the preparation of 1-alkyl, chloroalkyl, phenyl- and nitro-phenyl-phenanthridines in good yields starting, like Pictet and Hubert (*loc cit*), with *o*-amino-diphenyl Their chief interest lay in preparing the 1-ortho-, meta-, and para-amino-phenyl phenanthridines (i e 3 4-benzo-isoquinolines) of the following type which were expected to be physiologically active —

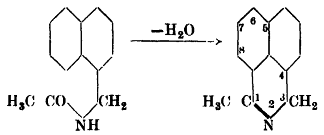


Recently, Braun and Nelles (*Ber*, 1937, *70*, 1760) have synthesised 6 7-benzo-isoquinoline reported previously by Phillips (*Ber*, 1894, *27*, 1923, 1895, *28*, 1658), in a more satisfactory manner, thus —



A survey of the literature relating to the investigations on the benzo-isoquinolines referred to above shows that our knowledge of these bodies is very incomplete at present The only methods entitled to serious consideration as constituting direct syntheses of isoquinolines from the naphthalene compounds are those of Pictet and Manevitch (*loc cit*) and of Simonsen and his co-workers (*loc cit*), but even in the latter cases, the products have not been characterised sufficiently fully A systematic study of the methods of preparation and properties of benzo-isoquinolines appears, therefore, to be highly desirable

The present investigation was undertaken with a view to prepare benzo-isoquinolines of the following type from the easily obtainable α-naphthyl methylamines, the C-atom in the peri position participating in the cyclisation —

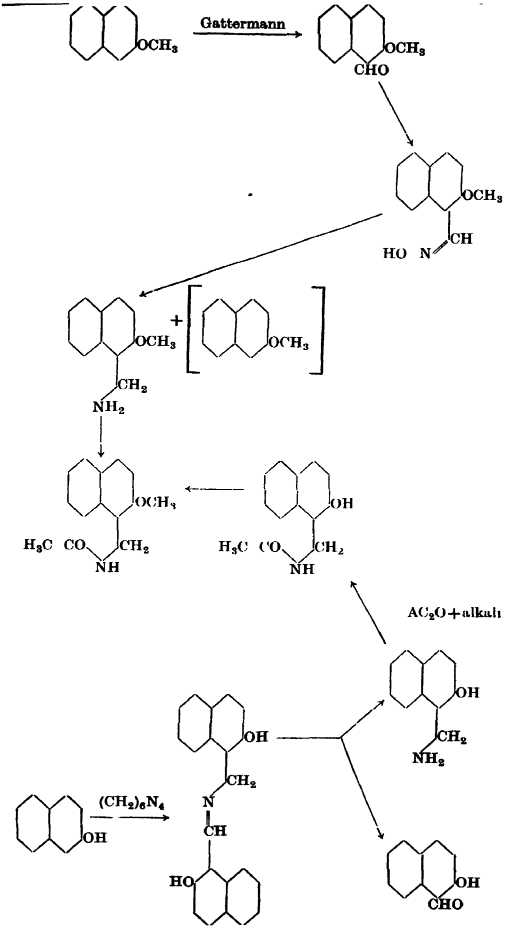


1, methyl-3, hydro-4 5 benzo-isoquinoline

Although compounds of the type Ar-C N C C have been known to resist attempts at cyclisation to isoquinoline derivatives (Cf Dey and Govindachari, *Arch Pharm*, 1937, 275, 383), it was hoped that the remarkable activity usually attributed to the peri C-atom in the naphthalene nucleus would counteract this reluctance to a great extent As examples of the ease with which peri-peri cyclic compounds are formed, may be mentioned the syntheses of substituted napthastyrils by Rule and Turner (*J Chem Soc*, 1935, 317) and of 7 8-dihydro-phenalone-9 by Meyer, Fischer and others (*Ber*, 1922, *55*, 1855) from naphthyl-1 propionyl chloride

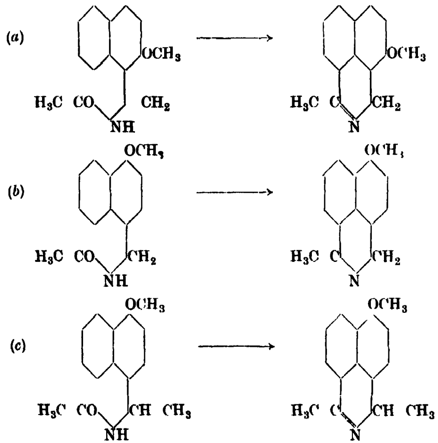
2- and 4-methoxy-naphthyl methylamines and 4-methoxy-naphthyl-α-methyl-methylamine were used as our starting materials

2-methoxy-naphthyl methylamine was obtained by the reduction of 2-methoxy naphthaldoxime (Brady and Goldstein, *J Chem Soc*, 1927, *130*, 1959), but the yield of the amine was much reduced by the simultaneous formation of considerable amounts of β-naphthol methyl ether, by the splitting off of the side chain in the α-position This rather unusual reaction has been noticed also with 2-hydroxy-naphthaldehyde by Betti and Mundici (*Gazetta*, 1906, *36*, 655) A more satisfactory process for the preparation of 2-hydroxy naphthyl methylamine was found in the hydrolysis, studied by Duff and Bills (*J Chem Soc*, 1934, 1307), of the addition compound of β-naphthol and urotropine The amine gave an N-acetyl derivative which on methylation formed the acetyl 2-methoxy-naphthyl methylamine in excellent yield The two methods are illustrated by the following scheme —


OCH3
Gattermann
OCH3
CHO
OCH3
HO N
CH
OCH3
CH2
NH2
+
OCH3
OCH3
H3C CO
CH2
NH
OH
H3C CO
CH2
NH
AC2O+alkali
OH
CH2
NH2
OH
CH2
N
CH
HO
(CH2)6N4
OH
OH
CHO

4, methoxy-naphthyl-methylamine was obtained without difficulty from *p*-methoxy-naphthaldoxime (Brady and Goldstein, *loc cit*) and 4, methoxy-naphthyl-α, methyl-methyl amine was prepared from *p*-methoxy-acetonaphthone oxime (Schneider and Kuhn, *Ber*, 1921, *54*, 2303), by reduction with sodium amalgam

The acetyl derivatives of these amines were subjected to the Bischler-Napieralsky reaction, peri-peri-benzo-isoquinolines being expected to be formed in the following manner —

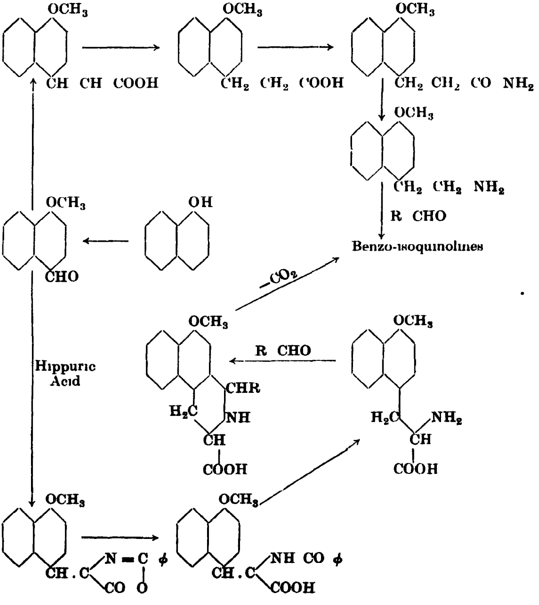


The action of phosphorus oxychloride with or without toluene or phosphorus pentoxide in boiling xylene led to the formation of only non-basic substances which could not be purified, while the action of phosphorus pentachloride in chloroform on the diacetyl and dibenzoyl derivatives of 2, hydroxy-naphthyl methylamine resulted in the formation of small quantities of crystalline substances containing chlorine but free from nitrogen It has not been possible to investigate the nature of these bodies on account of their poor yields

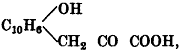
The failure to synthesise peri-peri-benzo-isoquinolines from substituted α, naphthyl-methylamines is thus parallel to the fruitless attempts made by other workers to obtain isoquinoline derivatives from bases of the benzylamine type (cf Mannich and Kuphal, *Arch Pharm*, 1912, *210*, 529; Staub, *Helv Chim*, 1922, *5*, 888, Dey and Govindachari, *Arch Pharm*, 1937, *275*, 383)

Other methods of synthesising these bodies were next explored, and attention was first directed to their preparation from naphthalene compounds having the side chain -C C N C -, a fair chance of success being anticipated from the results obtained in the syntheses of isoquinoline derivatives from the analogous β-phenyl ethylamines The simplest starting materials would obviously be the 1, and 2, naphthyl-β-ethylamines, derived from the α and β-naphthaldehydes Considering, however, the difficulties of preparing them (Meyer, Stieglitz, Fischer and others, *Ber*, 1922, *55*, 1855), it was decided to prepare substituted naphthyl ethylamines from other easily obtainable naphthalene compounds

Attempts were first made to prepare 4, methoxy-naphthyl-β-ethylamine by the usual method and the corresponding β-naphthyl alanine derivative by the method developed by Erlenmeyer and Kreutz (*Ann*, 1905, *337*, 205) for the syntheses of aminoacids These might be cyclised to the corresponding isoquinoline derivatives as indicated in the following scheme —



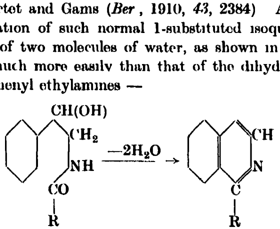
The conversion of α-naphthol into *p*-hydroxy-naphthaldehyde by the Gattermann reaction, and its transformation through the usual steps to 4-methoxy-naphthyl propionamide proceeded without difficulty, but the corresponding naphthyl ethylamine could under no circumstances be prepared by the usual Hoffmann reaction Again, on attempting to obtain β-naphthyl alanine by condensing *p*-methoxy-naphthaldehyde with hippuric acid, it was found that although the azlactone was easily formed, the reduction to *p*-hydroxy-naphthyl alanine by phosphorus and hydriodic acid by a method similar to that described by Gillespie and Snyder (Adam's Organic Syntheses, *14*, 80) was unsuccessful, a small amount of a nitrogen-free substance which, from analytical values, appeared to be *p*-hydroxy-naphthyl pyruvic acid,



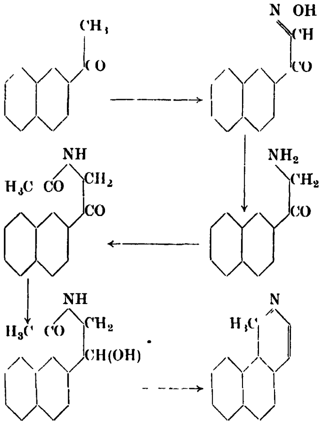
$$C_{10}H_6\begin{cases}OH\\CH_2\ CO\ COOH,\end{cases}$$

together with a considerable amount of tar were obtained

Attention was next turned to the syntheses of benzo-isoquinolines from naphthyl ethylamines with a β-hydroxyl group in the side chain by following the method of Pictet and Gams (*Ber*, 1910, *43*, 2384) According to these authors the formation of such normal 1-substituted isoquinolines from the carbinols by loss of two molecules of water, as shown in the scheme given below, proceeds much more easily than that of the dihydro-bases from acyl derivatives of β-phenyl ethylamines —

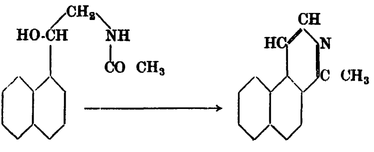


Experiments were, therefore, started with β-acetonaphthone, the cyclisation of N-acetyl-β-hydroxy-naphthyl-2-ethyl amine being considered to be easier on account of the reactivity of the α-carbon atom The course of the reactions was planned as follows —

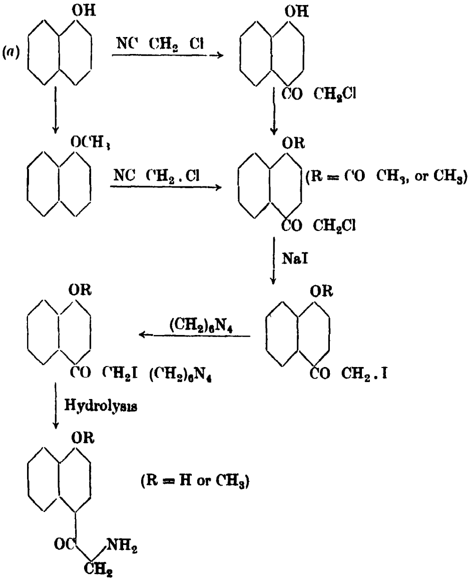


1-methyl-7 8-benzo-isoquinoline

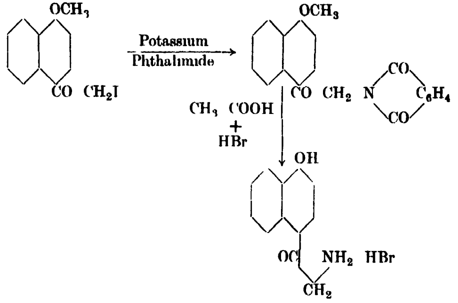
β-acetonaphthone was converted by the method of Claisen and Manasse (*Ber*, 1887, *20*, 656 and 2194) to its ω-iso-nitroso-derivative, which was then reduced to ω-amino-2, acetonaphthone hydrochloride according to the method of Rupe (*Ber*, 1895, *28*, 254) The salt, on treatment with acetic anhydride and excess of concentrated sodium hydroxide, gave the N-acetyl derivative which was reduced to N-acetyl-*β*-hydroxy-naphthyl-2-ethylamine (Pictet and Gams, *loc cit*) This, on treatment with phosphorus pentoxide in boiling xylene or toluene, yielded only yellow non-basic resins which could not be purified The failure to obtain the isoquinoline by this method led us to repeat carefully the work of Pictet and Manevitch (*Arch Sci Phys Nat* (4), 1913, *35*, 40) These workers started from *α*, aceto-naphthone and synthesised 1, methyl-5, 6-benzo-isoquinoline on exactly parallel lines, thus —



With but a few minor discrepancies in the melting points of the intermediate products, the reactions up to the last stage but one did not present any particular difficulty, but all our efforts to prepare the 1, methyl-5 6, benzo-isoquinoline, M P 95°–96°, reported by these workers, by treating the N-acetyl-β-hydroxy-naphthyl-1-ethylamine with phosphorus pentoxide in boiling xylene or toluene ended in failure Only coloured, non-basic oils and certain amounts of the original uncyclised substance were obtained Before arriving at any definite conclusions on this subject, it was considered necessary to try similar experiments with 4-methoxy acetonaphthone The exceedingly poor yield of the isonitroso ketone led to two alternative methods of preparing the ω-amino acetonaphthones (Mannich and Hahn, *Ber*, 1911, *44*, 1542) explained in the following schemes, being tried —



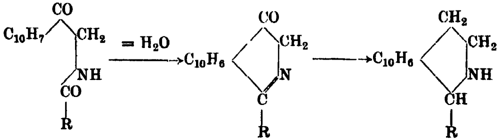
(*b*)



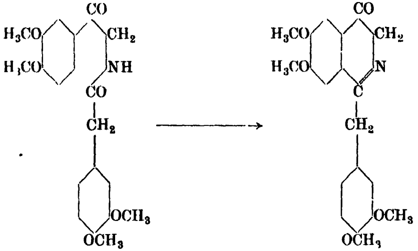
In scheme (*a*), the stages up to the preparation of 4-acetoxy and 4-methoxy-ω-iodoacetonaphthones proceeded without much difficulty, though the yields were poor, but these gave with hexamethylene tetramine, addition products which, unlike those obtained by Mannich and Hahn (*loc cit*), were insoluble in water and gave on treatment with alcoholic HCl, only sticky resins of a non-basic character

In scheme (*b*), following the method of Gabriel, it was possible to prepare 4-methoxy-naphthacyl phthalimide from 4-methoxy-ω-iodoacetonaphthone, but the *p*-hydroxy-ω-amino-acetonaphthone hydrobromide obtained by hydrolysis of the naphthacyl phthalimide could not be acetylated

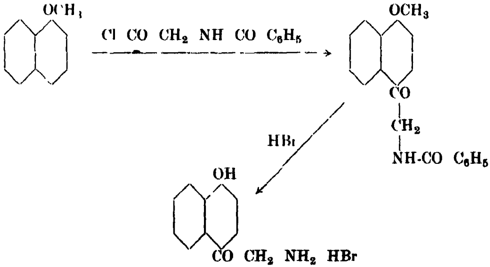
Due, therefore, either to the very poor yields of the products or to the failure of apparently simple reactions, further attempts in these directions had to be abandoned It was then proposed to attempt the cyclisation of compounds of the type $C_{10}H_7$ CO CH_2 NH COR (where R is an alkyl or aryl radical), when 4-keto-benzo-isoquinoline derivatives would be expected to be formed, and these could then be reduced to the tetrahydro isoquinolines, thus —



Although Perkin, Campbell and Haworth (*J Chem Soc*, 1926, 33) had failed to effect the cyclisation of formyl-ω-aminoacetoveratrone, and attributed their failure to the strong inhibiting influence of the carbonyl group in the side chain, it was hoped that the method might be applied with success to the preparation of benzoisoquinolones, particularly in view of the fact that Buck (*J. Am. Chem. Soc.*, 1930, *52*, 3610) was able to accomplish the synthesis in good yield of a 4-keto-isoquinoline from homoveratroyl-ω, amino-acetoveratrone according to the following scheme —

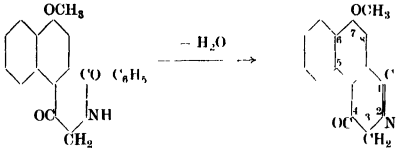


The preparation of N-acyl-ω-amino-acetonaphthones necessary for the syntheses of benzoisoquinolines involves a number of stages starting from the naphthyl methyl ketones. A simple method for the preparation of methoxybenzoyl-ω-aminoaceto-naphthone was found to consist in the condensation of α-naphthol methyl ether with hippuryl chloride in the presence of anhydrous aluminium chloride. Judging from analogy, the benzoyl amino acetyl group should have entered the naphthalene ring in the para-position to the methoxyl group as shown below —



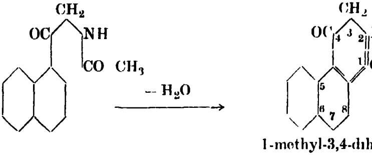
Attempts to oxidise this compound to *p*-methoxy naphthoic acid by the use of such agents as dilute nitric acid, alkaline hydrogen peroxide, potassium permanganate in acetone solution, etc., were unsuccessful, but on boiling with hydrobromic acid, the compound was hydrolysed to 4-hydroxy-ω-amino acetonaphthone hydrobromide which was identified with the sample obtained previously from 4-methoxy naphthacyl phthalimide (p 163)

Our expectation that 4-keto-benzoisoquinolines could be prepared by this method has now been fully realised, 1,phenyl-3,4-dihydro-4,keto-7,methoxy-5 6-benzoisoquinoline being obtained readily and in a satisfactory yield, when 4-methoxy-benzoyl-ω-amino-acetonaphthone was warmed with phosphorus oxychloride in toluene, thus

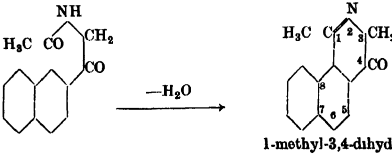


The reaction appears, therefore, to constitute a general method for the syntheses of 4-keto-isoquinolines

We followed up this successful cyclisation by studying the action of phosphorus oxychloride in toluene on the two acetyl ω-amino acetonaphthones, derived from α- and β-naphthyl methyl ketones The closure of the two isomeric compounds to the corresponding benzo-isoquinolines occurred with facility, as expected, according to the schemes given below



1-methyl-3,4-dihydro-4,keto-5 6,benzoisoquinoline

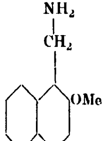


1-methyl-3,4-dihydro-4,keto-7 8,benzo-isoquinoline

All the three benzoisoquinolones are weak bases They do not dissolve easily in acids and can be completely extracted from acid solutions A number of salts of each have been prepared in order to characterise them in sufficient detail The keto group present in these compounds seems to be unreactive, and it has not been found possible to prepare any of the common derivatives The compounds have also resisted so far all attempts at reduction by the usual chemical methods.

EXPERIMENTAL

2,methoxy-naphthyl-methylamine,



2,methoxy-naphthaldehyde was prepared in the usual way from β-naphthol methyl ether, zinc cyanide, aluminium chloride and dry HCl 18 gms of the aldehyde crystallising from ligroin in pale yellow needles, M P 82°, were obtained from 20 gms of the methyl ether The *semicarbazone*, M P 213°, and the *oxime*, M P 154°-155°, were obtained in quantitative yields

2,methoxy-ω,nitro-naphthyl ethylene, prepared from the aldehyde, nitromethane and methyl alcoholic caustic potash, crystallised from glacial acetic acid in golden yellow needles, M P 141°

The reduction of the oxime to the amine was carried out as follows —

18 gms of 2-methoxy naphthaldoxime dissolved in 75 c c alcohol were treated with 400 gms of 4½% sodium amalgam added in small portions, with shaking The solution was kept faintly acidic throughout by periodical additions of 50% acetic acid and the temperature was maintained between 50°–70° by cooling at the tap The excess of alcohol and acetic acid was distilled off under reduced pressure on a boiling water-bath The distillate contained a steam-volatile, colourless crystalline solid (4 gms), M P 72° It was identified as β-naphthol methyl ether by the non-depression of its melting point when admixed with a pure specimen of β-naphthol methyl ether

The aqueous residue was repeatedly extracted with ether so as to free it from coloured oily non-basic impurities The aqueous solution was cooled in ice, strongly basified with excess of concentrated caustic soda and extracted with ether The ether extract was dried over anhydrous potassium carbonate and distilled The residue of 2-methoxy naphthyl methylamine solidified to a pale yellow crystalline solid M P 41°-42°, after sintering at 40° Yield, 6 gms

0 0932 gm of the base gave 6 1 c c nitrogen at 31° and 745 mm. pressure Found. N = 7 22%; $C_{12}H_{13}ON$ requires N = 7·49%

The hydrobromide melted at 246° (decomp)

The *acetyl derivative* crystallised from dilute alcohol in colourless, silky needles M P 172°

0 1161 gm gave 0 0664 gm of H_2O and 0 3106 gm of CO_2, also 0 1274 gm yielded 6 8 c c of nitrogen at 28° and 749 8 mm pressure

Found C = 72 95%, H = 6 35%, N = 6 26%

$C_{14}H_{15}O_2N$ requires C = 73 36%, H = 6 53%, N = 6 12%

The *benzoyl derivative* was prepared by adding benzoyl chloride to a solution of the base in dry benzene, evaporating the solvent and decomposing the excess of benzoyl chloride by standing with dilute caustic soda for a few minutes It crystallised from dilute alcohol in colourless needles, M P 155°

0 1860 gm gave 8 2 c c nitrogen at 29° and 747 9 mm pressure

Found N = 4 90%, $C_{19}H_{17}O_2N$ requires N = 4 81%

The picrate crystallised from acetic acid as yellow needles M P 215° (d)

0 1026 gm yielded 13 1 c c nitrogen at 30° and 748 mm pressure

Found N = 14 12%, $C_{18}H_{16}O_7N_4$ requires N = 14 00%

2-hydroxy-naphthyl methyl amine 10 gms of β-naphthol and 10 gms of hexamethylene tetramine in 40 c c glacial acetic acid were heated together under reflux at 100° for one hour The solution was concentrated to a small bulk by distilling the major portion of the solvent, cooled and the mixture of β-naphthol aldehyde and 2-hydroxy naphthyl methyl amine hydrochloride filtered The hydrochloride was separated by extracting the mixture repeatedly (five times) with a large volume of water at 50° and concentrating the extract. On cooling, the sparingly soluble hydrochloride separated out Yield, 5 gms M P 226°–230° (decomp) The insoluble residue, weighing 3-4 gms , was found to be nearly pure β-naphthol aldehyde The free *base* was obtained as a yellow crystalline solid on triturating the base hydrochloride with excess of ammonia or aqueous sodium carbonate M P 135°–138°

N-acetyl-2-hydroxy-naphthyl methyl amine was obtained in a quantitative yield by shaking a suspension of the base in water with acetic anhydride for a few minutes It crystallised from dilute alcohol in colourless needles M P 160°

0 0910 gm gave 0 0531 gm of H_2O and 0 2420 gm CO_2.

Found C = 72 52%, H = 6 47%

$C_{13}H_{13}O_2N$ requires C = 72 56%, H = 6 07%

N-acetyl-2,methoxy-naphthyl methyl amine was obtained in excellent yield by shaking up a solution of N-acetyl-2,hydroxy-naphthyl methyl amine in dilute caustic soda with dimethyl sulphate for a few minutes It crystallised from dilute alcohol as colourless silky needles melting at 172°, identical with that prepared from 2,methoxy-naphthyl methyl amine (see above).

The N-acetyl-2,acetoxy-naphthyl methyl amine, obtained by shaking the hydroxy-base with excess of acetic anhydride and alkali, crystallised from alcohol as colourless needles M P 171°-172°.

0 1022 gm gave 0 2629 gm CO_2 and 0 0542 gm H_2O, 0 1852 gm gave 9 8 c c nitrogen at 29° and 747 9 mm pressure

Found $C = 70\ 17\%$, $H = 5\ 89\%$, $N = 5\ 88\%$

$C_{15}H_{15}O_3N$ requires $C = 70\ 04\%$, $H = 5\ 84\%$, $N = 5\ 45\%$

The N-benzoyl-2,benzoyloxy-naphthyl methyl amine, crystallised from acetic acid as colourless prisms M P 212°

0 1262 gm of substance gave 0 3648 gm CO_2 and 0 0568 gm H_2O

Found $C = 78\ 84\%$, $H = 4\ 99\%$

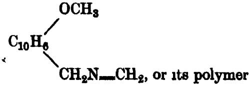
$C_{25}H_{19}O_3N$ requires $C = 78\ 74\%$, $H = 5\ 00\%$

ATTEMPTED CYCLISATION OF ACETYL, 2-METHOXY-NAPHTHYL METHYL AMINE

(*a*) *By the method of Bischler and Napieralsky* 1 gm of the acetyl derivative of the amine was treated with 5 c c phosphoryl chloride, when it went into a clear solution This was heated under reflux on a boiling water-bath for one hour with the exclusion of moisture The dark coloured solution was cooled and poured on to crushed ice A dark oil separated out which gradually solidified The mixture was allowed to attain the room temperature and then filtered The filtrate was strongly cooled in ice, basified with excess of concentrated alkali and the clear aqueous solution repeatedly extracted with ether The ether extract, on drying and distilling, left no residue The solid product of the reaction obtained above was insoluble in dilute acids and contained phosphorus It could not be purified further

The same result was obtained when toluene was used as a diluent and phosphorus pentoxide or phosphorus pentachloride were substituted as the cyclising agents

(*b*) *By the method of Decker and Becker* 1 gm of the amine dissolved in 2 c c of methanol was heated with 2 c c of formalin at 60°-70° for 20 minutes when a thick reddish brown oil separated out The supernatant liquid was decanted off, the residual syrup freed from formalin by washing repeatedly with small amounts of water, and then treated with 4-5 c c of strong HCl The mixture was warmed on the boiling water-bath for 10 to 15 minutes, diluted with water and filtered The aqueous solution, on cooling, deposited an orange coloured solid (0 8 gm) which was found to be only a neutral product, with no definite melting point, and which on prolonged heating with concentrated HCl split off formaldehyde and gave the original amine on basification and extraction with ether The product was therefore believed to be the N-formylidene compound,



$C_{10}H_6(OCH_3)CH_2N{=}CH_2$, or its polymer

The original aqueous acid filtrate from this compound did not yield any basic product on working up in the usual way The same result was obtained when methylal was substituted for formalin in the above experiment

Action of PCl_5 on the diacetyl derivative of 2-hydroxy-naphthyl methyl amine 1 gm of the substance in chloroform was treated with 4 gms of PCl_5 and allowed to stand overnight and then warmed at 70° for an hour The mixture was poured on to crushed ice and the resulting oil kept in contact with diluted alcohol when it slowly solidified Crystallisation from alcohol gave colourless needles M P 182° The substance contained chlorine but no nitrogen It was analysed but could not be investigated further

0 880 gm gave 0 2210 gm CO_2 and 0 0342 gm H_2O, 0 1425 gm of substance gave 0 1187 gm AgCl

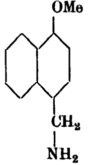
Found C = 68 48%, H = 4 32%, Cl = 20 59%

Action of PCl_5 on the dibenzoyl derivative of 2-hydroxy-naphthyl methyl amine A mixture of 1 gm of substance and 1 gm of PCl_5 in chloroform was allowed to stand overnight, the chloroform evaporated away at the ordinary temperature and the residue treated with ice, when an oil separated out which solidified on treatment with a little alcohol It was recrystallised from dilute alcohol Colourless needles M P 126° The substance, containing chlorine but no nitrogen, appeared to be similar to the previous compound

0 1008 gm of substance gave 0 2077 gm CO_2 and 0 0616 gm H_2O. 0 1292 gm of substance yielded 0 0981 gm of AgCl

Found C = 56 22%, H = 6 79%, Cl = 12 82%

4,methoxy-naphthyl methyl amine



4,hydroxy-naphthaldehyde was prepared by the method of Adams and Levine (*J Amer Chem Soc*, 1923, *45*, 2373) 17 gms of colourless needles, M P 182°, were obtained from 20 gms of α-naphthol

The methyl ether (Brady and Goldstein, *J Chem Soc*, 1927, *130*, 1959) was obtained by methylation with methyl sulphate and alkali as an oil, B P 185°-190°/10 mm in a yield of 70 per cent of theory

4,methoxy-naphthaldoxime (Schopf and Bayerle, *Ann*, 1934, *513*, 190) was readily obtained in a quantitative yield by refluxing the aldehyde with hydroxylamine hydrochloride and alkali in alcoholic solution It crystallised from benzene as colourless needles, M.P 108°.

3 5 gms of the oxime, dissolved in 20 c c of alcohol, were treated with small portions of 4% sodium amalgam (100 gms) with shaking. The solution

was kept faintly acidic throughout by periodical addition of 50% acetic acid and the temperature of the mixture was maintained between 50°–70° by cooling under the tap The excess of alcohol and acetic acid was distilled off under reduced pressure over a boiling water-bath The residual aqueous solution was repeatedly exhausted with chloroform (120 c c) with a view to free it from non-basic impurities The acid solution on working up in the usual way did not yield any basic product Evaporation of the chloroform extract after drying over calcium chloride, however, yielded 2 6 gms of a crystalline solid, which was found to be the acetate of the base It was recrystallised from chloroform as colourless rods M P 160°

0 1396 gm (dried at 100°) yielded 7 4 c c nitrogen at 29° and 745 mm. pressure.

Found N = 5·89%, $C_{14}H_{17}O_3N$ requires N = 5 67%

The 4-methoxy-naphthyl methyl amine was obtained as a thick oil by basifying the acetate

The hydrochloride crystallised from water as long, colourless needles, M P. 215° (decomp)

0 1823 gm (dried at 100°) yielded 0 1180 gm of AgCl

Found Cl = 16 01%, $C_{12}H_{14}ONCl$ requires Cl = 15 86%

The acetyl derivative crystallised from alcohol as colourless plates M P 136°

0 01740 gm gave 0·04659 gm CO_2 and 0 00996 gm. H_2O

0 1310 gm yielded 7 3 c c nitrogen at 29° and 745 mm pressure

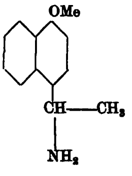
Found C = 73 03%, H = 6 36%, N = 6 20%

$C_{14}H_{15}O_2N$ requires C = 73 36%, H = 6 53%, N = 6 12%

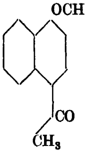
The *picrate* crystallised from glacial acetic acid as golden yellow rods M P 240°–243° (decomp)

Attempted cyclisation of acetyl-4-methoxy-naphthyl methyl amine 1 gm of the acetyl derivative in 4 c c toluene was gently refluxed with 3 c c phosphoryl chloride on the sand-bath for an hour, with the exclusion of moisture The dark red solution was cooled, poured on to crushed ice, allowed to come to the room temperature with stirring and exhausted with chloroform so as to free it from non-basic impurities. The aqueous acid solution, on working up in the usual way, yielded a reddish brown, non-basic resin which could not be purified.

4,methoxy-naphthyl-α,methyl methyl amine



4,methoxy-acetonaphthone This ketone has been formerly prepared by Gattermann, Erhardt and Maisch (*Ber*, 1890, *23*, 1208) by the action of acetyl chloride on α,naphthyl methyl ether in the presence of anhydrous aluminium chloride Later, Schneider and Kuhn (*Ber*, 1921, *54*, 2305) prepared the ketone in a better yield by using a sulphuric acid-acetic anhydride mixture The following method is found to give a better yield and a purer product



A mixture of 40 gms of α-naphthyl methyl ether (Witt and Schneider, *Ber*, 1901, *34*, 3173) in 100 c c carbon-disulphide and 40 gms of anhydrous aluminium chloride was treated in the course of an hour with 40 c c acetic anhydride (1 5 mols) added little by little with shaking and with the exclusion of moisture The mixture was gently refluxed on the water-bath for three hours and allowed to stand overnight The mixture was then poured on to crushed ice, acidified with a large excess of concentrated HCl, so as to dissolve the precipitated aluminium hydroxide and repeatedly extracted with ether The ether extract was washed with dilute caustic soda followed by water several times, the ether driven off and the residue then distilled under ordinary pressure The portion boiling between 300°–350° crystallised on cooling The *p*-methoxy acetonaphthone, which was contaminated with small amounts of α-naphthol methyl ether, was obtained pure after washing with a little petroleum ether M P 69°–70° Yield, 22 gms

4-methoxy acetonaphthone oxime (Schneider and Kuhn, *loc cit*) 5 gms of the ketone, 1 8 gms hydroxylamine hydrochloride (1 25 mols) and 3 gms barium carbonate were heated together in 60 c c alcohol under reflux on the water-bath for five hours The mixture was filtered hot and the $BaCO_3$ washed twice with small amounts of hot alcohol The alcoholic solution was concentrated to a fourth of its volume and diluted with 5 c c water, when the oxime crystallised out as colourless needles M P. 122°-123°, after sintering at 120° Yield, 4 9 gms.

4-methoxy-naphthyl-α-methyl methyl amine 4 8 gms of *p*-methoxy acetonaphthone oxime dissolved in 30 c c. alcohol were treated with 150 gms of 4% sodium amalgam, added little by little with shaking The reaction mixture was kept faintly acidic throughout by periodical addition of 50% acetic acid The temperature was maintained between 50°–70°, by cooling under the tap whenever necessary. The mixture was tapped off from the mercury, filtered and the excess of alcohol and acetic acid removed by distilling under reduced pressure over a boiling water-bath The aqueous solution was cooled, basified strongly and repeatedly extracted with chloroform The chloroform extract was then exhausted with dilute acetic acid The acid extract on treatment with an excess of concentrated HCl deposited the sparingly soluble hydrochloride It was recrystallised from boiling water Colourless, hexagonal plates M P 270° Yield, 3 gms

The free base was obtained as a thick pale yellow oil by treatment of the hydrochloride with alkali

0 1082 gm of the oil gave 6 8 c c nitrogen at 31° and 745 1 mm pressure

Found N = 6 90%, $C_{13}H_{15}ON$ requires N = 6 96%

0 2440 gm of the hydrochloride gave 0 1479 gm of AgCl

Found Cl = 15 00%, $C_{13}H_{15}ONCl$ requires Cl = 14 93%

The acetyl derivative crystallised from dilute alcohol as colourless, silky needles M P 174°

0 01224 gm gave 0 03427 gm CO_2 and 0 00732 gm H_2O 0 1142 gm yielded 5 9 c c nitrogen at 30° and 748 mm pressure

Found C = 74 60%, H = 6 63%, N = 5 73%

$C_{15}H_{17}O_2N$ requires C = 74 08%, H = 6 99%, N = 5 76%

The benzoyl derivative crystallised from a mixture of methanol and acetic acid as colourless, silky needles M P. 198°

0 0952 gm gave 3 9 c c nitrogen at 30° and 748 mm pressure

Found N = 4·54%

$C_{20}H_{19}O_2N$ requires N = 4 59%

The picrate crystallised from glacial acetic acid as golden yellow prismatic needles M P 255° (d).

Attempted cyclisation of acetyl, 4-methoxy-naphthyl-α-methyl methyl amine. 1 gm of the acetyl derivative was heated with 5 c c $POCl_3$ on the boiling water-bath for two hours, with the exclusion of moisture The whole of the amide went into solution The solution was cooled and poured on to crushed ice, when there was a large separation of a dark green resinous product insoluble in dilute acid solution The mixture was extracted with chloroform so as to free it from this non-basic impurity The residual dark green resin obtained from the chloroform extract could not be purified The aqueous solution on working up in the usual way did not yield any basic product.

The use of toluene as a diluent in the above reaction also led to the same result

Attempted synthesis of substituted naphthyl-β-methyl-amines from α-naphthol-4,aldehyde.

4,carbethoxy-naphthaldehyde 1 gm of 4-hydroxy-naphthaldehyde dissolved in dilute NaOH (1N) was treated in the cold with 1 c c ethyl chloroformic ester and shaken for about 20 minutes, when a dark brown oil resulted This on treatment with methanol and rubbing solidified to a brown mass which crystallised from alcohol as colourless needles M P 89° Yield 0·7 gm

0 01482 gm gave 0 03805 gm CO_2 and 0 00680 gm H_2O

Found C = 70 03%, H = 5 10%, $C_{14}H_{12}O_4$ requires C = 68 85%, H = 4 92%

Attempts to prepare 4-carbethoxy naphthyl acrylic acid by heating the aldehyde and malonic acid with pyridine and piperidine in the usual manner were unsuccessful The product was found to be the *p*-hydroxy-naphthaldehyde M P 182°

A similar failure was met with on attempting to prepare the nitrostyrene derivative by condensation with nitromethane under the usual conditions

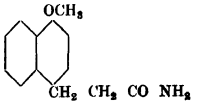
4-methoxy-naphthyl acrylic acid This acid has been formerly obtained by Rousset (*Bull Soc Chim*, 1904, *17*, 307) in 20% yield by heating 4-methoxy naphthaldehyde with acetic anhydride and sodium acetate at 180° for 36 hours The following method is simpler and gives a nearly quantitative yield of the acid

9 gms of the methoxy naphthaldehyde, 9 8 gms dry malonic acid (1 5 mols), 8 3 c c pyridine (1 5 mols) and 4 drops of piperidine were heated together under reflux on the boiling water-bath for an hour, followed by gentle boiling for 15 minutes over a naked flame The mixture was cooled and poured into excess of ice-cold dilute hydrochloric acid The separated solid was filtered, dried on the plate and crystallised from toluene Colourless needles, M P 215°–217° Yield, 8 5 gms

4-methoxy naphthyl propionic acid This has been prepared previously by Windaus (*Ber*, 1917, *50*, 1120) and by Ruhemann and Levy (*ibid*, 1920, *558*, 265) by catalytic hydrogenation of the acrylic acid

8 5 gms of the acrylic acid was reduced by 200 gms of 3% sodium amalgam in neutral or faintly alkaline solution at the room temperature The alkaline solution was filtered, cooled and acidified with concentrated HCl and the precipitated propionic acid crystallised from dilute alcohol Colourless needles, M P 163°–165° Yield, 7 5 gms

4-methoxy naphthyl propionamide A current of dry ammonia gas was passed through 7 2 gms. of the molten acid heated in an oil-bath at 165°–170° for 5-6 hours The red oily residue was dissolved in 25 c c of a saturated solution of sodium bicarbonate, when an oil separated out This solidified slowly on treatment with a little alcohol and rubbing with a rod The alkaline mother-liquor on concentration on the water-bath gave some more of the amide. The amide crystallised from dilute alcohol as colourless needles, M P. 113° Yield, 2 6 gms. Weight of recovered acid from the bicarbonate solution, 1 8 gm

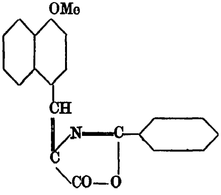


0·1944 gm gave 10 8 c c. nitrogen at 31° and 743 3 mm pressure.
Found N = 6 10%, $C_{14}H_{15}O_2N$ requires N = 6 11%

Several attempts were made to prepare 4-methoxy naphthyl ethylamine from the propionamide by the Hoffmann reaction but they were all unsuccessful, only non-basic resinous matter being obtained

EXPERIMENTS TOWARDS THE SYNTHESIS OF A β-NAPHTHYL ALANINE

Azlactone of α-benzoylamino-p-methoxy-naphthyl acrylic acid 10 gms of 4-methoxy naphthaldehyde, 6 gms of dry hippuric acid (1 2 mols), 2 7 gms freshly fused sodium acetate (1 2 mols) and 8 c c pure acetic anhydride (3 mols) were slowly heated together on the oil-bath at 110° The mixture slightly liquefied at first and then solidified to an orange-red crystalline mass After continuing the heating for another 2 hours, 25 c c alcohol were added, the mass broken up, filtered and washed with 15 c c alcohol (3 lots) followed by 10 c c of boiling water The crystalline azlactone was obtained in a high state of purity Recrystallisation from ligroin gave orange-red needles, M P 188°. Yield, 7·5 gms



0·1333 gm. gave 5 3 c c nitrogen at 32° and 740 mm
Found N = 4 27%, $C_{21}H_{15}O_3N$ requires N = 4 22%

Attempted preparation of β-4-hydroxy-naphthyl alanine (Gillespie and Snyder, Adam's Organic Synthesis, *14*, 80)

A mixture of 3 gms of the azlactone, 3 gms of red phosphorus and 16 c c acetic anhydride was treated with 25 c c of 50% hydriodic acid, during the course of half an hour with good shaking The mixture was refluxed for four hours, cooled, filtered and the phosphorus washed twice with small quantities of acetic acid The filtrate was evaporated on the water-bath under reduced pressure, 20 c c of water added and the solution evaporated again to dryness. The residue was extracted with small amounts of boiling water The filtrate, on cooling, yielded colourless plate-shaped crystals of an acid which contained no nitrogen M P. 122° Yield, 0·2 gm The insoluble tarry residue gave no evidence of the presence of the expected *dl*-β-4-hydroxy-naphthyl alanine.

The acid, on analysis, appeared to be the 4,hydroxy-naphthyl-pyruvic acid.

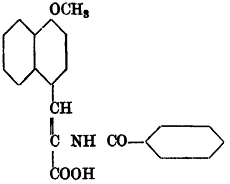
0·01258 gm gave 0·03019 gm CO_2 and 0·000507 gm H_2O

Found: C = 65·45%, H = 4·48%

$C_{13}H_{10}O_4$ ½H_2O requires C = 65·27%, H = 4·60%

α-benzoyl amino-p-methoxy naphthyl acrylic acid

6 gms of the azlactone suspended in 1,000 c c water was stirred mechanically on the boiling water-bath and treated with 1 gm. of NaOH in 10 c c of water The mixture was heated with stirring for 4-5 hours and filtered hot from a considerable amount of the unchanged azlactone, cooled, acidified with dilute HCl and filtered The acrylic acid crystallised from glacial acetic acid as pale yellow prismatic needles M P 230° Yield, 3 gms Weight of recovered azlactone, 2·5 gms



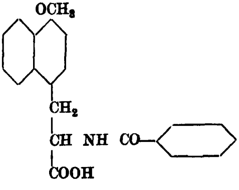
0·01756 gm. gave 0·04687 gm CO_2 and 0·00701 gm H_2O

Found C = 72·80%, H = 72·63%; H = 4·90%

$C_{21}H_{17}O_4N$ requires C = 72·63%, H = 4·90%

α-benzoylamino-p-methoxy-naphthyl propionic acid

2 gms of the acid suspended in 100 c c water in a separating funnel was treated with dilute caustic soda till just dissolved, and 75 gms of 3% sodium amalgam were added little by little with shaking in the course of about an hour. The reaction-mixture was maintained faintly alkaline or neutral by



adding periodically small amounts of dilute acetic acid The aqueous solution was filtered and acidified with dilute HCl, when an oil separated which soon solidified The mixture was allowed to stand overnight and filtered and the reduced acid crystallised from toluene Small white needles M P 166°–168° Yield, 0 21 gm

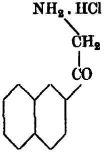
0 01252 gm gave 0 03306 gm CO_2 and 0 00631 gm H_2O
Found C = 72 01%, H = 5 6%
$C_{21}H_{19}O_4N$ requires C = 72 21%, H = 5 45%

SYNTHESIS OF N-ACETYL-β-HYDROXY-NAPHTHYL-2-ETHYLAMINE AND ATTEMPTED CYCLISATION OF THE SAME

Isonitroso-2-acetonaphthone A mixture of 2 7 gms of sodium dissolved in 50 c c absolute alcohol and 15 gms of β-acetonaphthone strongly cooled in a freezing mixture was treated with 16 2 c c of freshly prepared amyl nitrite (1 25 mols) added drop by drop with good shaking in the course of an hour and a half The mixture was tightly corked up and allowed to stand at 0° for three days The orange-red sodium salt of the ω-isonitroso ketone was filtered and repeatedly washed with absolute alcohol and ether The aqueous solution of the sodium salt was filtered, cooled and acidified with excess of dilute acetic acid The yield of the isonitroso ketone was 8 6 gms or 50% of theory (M P 90°-91°) It was crystallised from alcohol Pale yellow needles, M P 93°-94°

0 2240 gm gave 14 7 c c nitrogen at 30·5° and 746 7 mm pressure
Found N = 7 22%, $C_{12}H_9O_2N$ requires N = 7 04%

ω-amino-2-acetonaphthone hydrochloride A mixture of 30 gms of anhydrous stannous chloride and 100 c c absolute alcohol was saturated with dry HCl gas at −5°, a solution of 8 6 gms of isonitroso acetonaphthone in 30 c c absolute alcohol added in three instalments, and the solution saturated again with HCl gas at −5° The mixture was allowed to attain room temperature and stand overnight The white crystalline tin double compound was filtered, washed with a little alcohol, dissolved in hot water (about 150 c c) and decomposed twice with sulphuretted hydrogen The colourless aqueous filtrate was concentrated to a small bulk on the water-bath and finally evaporated to dryness in a vacuum over sulphuric acid The residue of hydro-

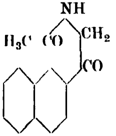


chloride was recrystallised twice from alcohol Colourless plates, M P 220° (decomp). Yield, 4 6 gms or 49% of theory

0 2166 gm gave 0 1447 gm of AgCl
Found. Cl = 16 50%
$C_{12}H_{12}ONCl$ requires Cl = 16 01%

The picrate crystallised from glacial acetic acid as golden yellow prismatic needles M P 189° (decomp)

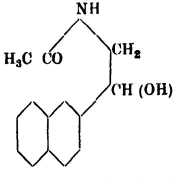
Acetyl-ω-amino-2-acetonaphthone 4 6 gms of the hydrochloride, dissolved in water, were treated with 5 c c acetic anhydride and excess of concentrated NaOH Much heat was evolved and the crystalline acetyl compound separated out in the course of about 15 minutes Recrystallisation from alcohol gave colourless needles M P 132°-133° Yield, 4 6 gms



0·01470 gm gave 0 04010 gm CO_2 and 0 00796 gm H_2O, 0 1482 gm gave 8 4 c c nitrogen at 30 5° and 746·7 mm pressure

Found: C = 74 4%; H = 6 01%, N = 6 26%
$C_{14}H_{13}O_2N$ requires C = 74 0%, H = 5 73%, N = 6·17%

N-acetyl-β-hydroxy naphthyl-2-ethylamine 4 6 gms of the above amide dissolved in 40 c c absolute alcohol was treated with small portions of 3% sodium amalgam (about 3 mols) with good shaking Acetic acid was added from time to time to keep the medium faintly acidic and the temperature maintained between 50°-60° by cooling now and then under the tap The alcohol-acetic acid solution was concentrated to about 15 c c and diluted with 100 c c. water and the separated carbinol filtered after an hour. Two crystallisations from benzene gave thin hairy crystals M P. 96°. Yield, 3 4 gms., or 70% of theory.



0·01517 gm gave 0·04250 gm CO_2 and 0·00908 gm H_2O
Found C = 73 69%, H = 6 42%
$C_{14}H_{15}O_2N$ requires C = 73 40%, H = 6 55%

Picrate of β-hydroxy-naphthyl-2-ethylamine Acetyl-hydroxy-naphthyl ethylamine was boiled with dilute HCl (4N) for a few minutes, the solution filtered and treated with dilute alkali till faintly acidic and then treated with a slight excess of saturated picric acid solution The precipitated picrate crystallised from absolute alcohol as stout yellow prisms, decomposing suddenly at 334° with a feeble explosion

Attempted cyclisation of acetyl-β-hydroxy-naphthyl-2-ethylamine 1 gm of acetyl β-hydroxy-naphthyl ethylamine was dissolved in 15 c c dry xylene by warming and the solution added to a flask containing 5 gms of phosphorus pentoxide The mixture was gently boiled in an oil-bath for about 15 minutes when a semi-solid, dark yellow mass appeared at the bottom of the flask The heating was continued for another quarter of an hour and the supernatant liquid decanted off while it was still warm The residue was treated with crushed ice and the mixture allowed to attain the room temperature slowly with stirring There was a good separation of a yellowish non-basic resinous product which could not be purified, while the aqueous acid filtrate gave no trace of any basic material when worked up in the usual manner

The reaction was repeated under different conditions using toluene as a solvent and also phosphorus pentachloride in chloroform with virtually the same result

PREPARATION OF N-ACETYL-β-HYDROXY-NAPHTHYL-1-ETHYLAMINE AND ATTEMPTED CYCLISATION TO 1-METHYL-5 6-BENZOISOQUINOLINE, REPORTED BY PICTET AND MANEVITCH (*Arch Sci Phys Nat* (4), 1913, *35*, 40)

ω-amino-α-acetonaphthone hydrochloride A mixture of 6 8 gms of sodium (1 25 mols) dissolved in 150 c c absolute methanol and 40 gms of α-naphthyl methyl ketone strongly cooled in a freezing mixture was treated with 32 4 c c freshly prepared amyl nitrite (1 mol) added drop by drop with good shaking, in the course of two hours The mixture was tightly corked up and allowed to stand at 0° for three days As the separation of the orange-red sodium salt was very small the isonitroso ketone was not isolated Instead, the solution was added drop by drop to a strongly cooled solution of 50 gms of $SnCl_2$ in 100 c c absolute methanol saturated with HCl gas The mixture was again saturated with HCl at 0° and allowed to stand overnight The tin double compound was filtered and washed with alcohol, followed by water It was then suspended in 400 c c hot water containing HCl and repeatedly decomposed with H_2S The hot aqueous filtrate on slight concentration soon deposited almost the whole of the sparingly soluble hydrochloride as crystals It was obtained pure by one crystallisation from boiling water M P 258°-259° (Pictet and Manevitch gave M.P 245°-250°) Yield, 9·6 gms.

Acetyl-ω-amino-1-acetonaphthone A suspension of 5 gms of the powdered hydrochloride in 40 c c water and 5 c c acetic anhydride was strongly cooled in ice and shaken with excess of concentrated caustic soda, added gradually The crystalline acetyl derivative soon separated out It was recrystallised from dilute alcohol as colourless needles, M P 102° Yield, 4 8 gms

N-acetyl-β-hydroxy-naphthyl-1-ethylamine 3 5 gms of the above amide dissolved in 30 c c of absolute methanol was treated with small portions of 50 gms of 3% sodium amalgam and the mixture worked up in the usual way Two crystallisations from toluene gave colourless plates, M P 150°-151° (Pictet and Manevitch give M P 145°-146°) Yield, 1 4 gms

Attempted cyclisation of acetyl-β-hydroxy-naphthyl-1-ethylamine 0 7 gm of the above carbinol dissolved in 12 c c warm, dry xylene was added to a flask containing 3 4 gms of P_2O_5 The mixture was gently refluxed in an oil-bath for 20 minutes with the exclusion of moisture The warm supernatant liquid was decanted off and the residue treated with crushed ice and the mixture slowly allowed to come to the room temperature with stirring As observed by Pictet and Manevitch, a clear solution did not result, but there remained always a certain quantity of undissolved resinous material This was separated by repeated extractions with chloroform in which it dissolved and from which it was recovered by evaporation On examination it proved to be non-basic The clear aqueous acid solution was strongly cooled, basified with excess of concentrated NaOH and repeatedly extracted with chloroform The chloroform extract was dried over K_2CO_3 and distilled 0 15 gm of a crystalline solid, M P 148°-150°, was left behind This, on crystallisation from toluene, melted at 150°-151°, and did not lower the melting point or the original uncyclised carbinol

Repetition of the experiment under other conditions led to the same result

EXPERIMENTS TOWARDS THE PREPARATION OF A SUBSTITUTED ω-AMINO-ACETONAPHTHONE STARTING FROM α-NAPHTHOL

α-naphthol methyl ether was prepared from α-naphthol by the method of Witt and Schneider (*Ber*, 1904, *34*, 3173) 40 gms of the ether, B P 264°, were obtained from 50 gms of naphthol

4-methoxy acetonaphthone was prepared by the method described before (p 153)

4-methoxy-isonitroso-acetonaphthone (Madinaveitia, *Bull Soc Chim*, 1919, *25*, 601) was prepared as usual from a mixture of 4 5 gms sodium in 100 c c alcohol, 22 gms finely powdered *p*-methoxy acetonaphthone and 18 c c freshly prepared amyl nitrite (1·25 mols)

Yield of the crude product, 3·5 gms Weight of unreacted ketone recovered, 6 gms The isonitroso ketone crystallised from alcohol as greenish yellow needles, M.P. 161°.

Preparation of 4-hydroxy-ω-chloracetonaphthone (Houben, *Ber*, 1926, *59*, 2876) A mixture of 10 gms of α-naphthol, 5 3 gms chloracetonitrile (1 mol) in 25 c c anhydrous ether and 10 gms anhydrous zinc chloride was saturated with dry HCl gas at 0°, with the exclusion of moisture The ketimine hydrochloride separated out as a greenish yellow solid in about half an hour The supernatant liquid was decanted off and the residue washed twice with small amounts of dry ether The solid was dissolved in 100 c c warm water, heated to boiling and allowed to stand for an hour The separated 4-hydroxy-ω-chloracetonaphthone was crystallised from alcohol White, silky needles M P 184° Yield, 7 5 gms

4-acetoxy-ω-chloracetonaphthone was prepared by boiling the hydroxy compound with acetic anhydride and a drop of pyridine, till dissolved, and pouring the solution into excess of water The oil, which separated out, soon solidified It crystallised from alcohol as colourless hexagonal plates M P 118°

0 2166 gm of substance gave 0 2128 gm AgCl

Found Cl = 13 66%, $C_{14}H_{11}O_3Cl$ requires Cl = 13 51%

4-hydroxy-ω-iodoacetonaphthone 4 gms of 4-hydroxy-ω-chloracetonaphthone dissolved in acetone was treated with a solution of 3 gms NaI in acetone and the mixture allowed to stand overnight and poured into excess of ice water, when a thick oil separated out The supernatant aqueous layer was poured off and the residual oil treated with ligroin After rubbing with a rod, it solidified to a pale yellow solid, which was filtered and washed well with ligroin It crystallised from toluene as pale yellow prismatic needles

0 1376 gm of substance gave 0 1048 gm AgI

Found I = 41 00%, $C_{12}H_9O_2I$ requires I = 40 70%

4-acetoxy-ω-iodoacetonaphthone was prepared similarly from 4,acetoxy-ω-chloroacetonaphthone It crystallised from alcohol as pale yellow plates M P 73° Yield, quantitative

0·1076 gm of substance gave 0·1022 gm of AgI.

Found I = 35 99%; $C_{14}H_{11}O_3I$ requires I = 35 86%

Addition compound of 4-acetoxy-ω-iodoacetonaphthone and urotropine A solution of 5 gms of 4-acetoxy-ω-iodoacetonaphthone in dry chloroform was treated with a solution of 2 gms of urotropine in chloroform and the mixture allowed to stand at the room temperature for three days The separated yellow crystalline solid was filtered, washed with chloroform and dried M P 169°-170° Yield, 3 5 gms The product was insoluble even in boiling water

0 1422 gm of the substance gave 14·9 c c nitrogen at 31° and 742 mm. pressure

Found N = 11 51%, $C_{20}H_{23}O_3N$ requires N = 11 33%

Attempts to prepare 4-hydroxy-ω-aminoacetonaphthone from the above were unsuccessful

4-methoxy-ω-chloracetonaphthone This has been obtained by Madinaveitia and Puyal (*Anales Soc espan fis quim*, 1919, *17*, 125) by the action of Cl CH_2 CO Cl on α-naphthyl methyl ether and reported to melt at 70° It is now found to be more convenient to prepare the ketone by the Hoesch reaction

A mixture of 10 gms of α-naphthyl methyl ether, 5 gms of chloracetonitrile in 30 c c anhydrous ether and 10 gms of anhydrous $AlCl_3$ was saturated with dry HCl gas at 0° The ketimine hydrochloride separated as a thick oil which slowly solidified after a number of hours The reaction mixture was allowed to stand overnight, the ether poured off and the residual solid washed twice with ether It was then decomposed by boiling with 100 c c water for a few minutes when a brownish oil separated out The aqueous layer was decanted off and the oil allowed to stand in the cold with excess of petroleum ether and rubbed The methoxy-chloracetonaphthone solidified to a yellow solid and crystallised from alcohol in colourless needles M P 75° Yield, 7 gms

0 1320 gm of substance gave 0 0822 gm of AgCl

Found Cl = 15 39%, $C_{13}H_{11}O_2Cl$ requires Cl = 15 12%

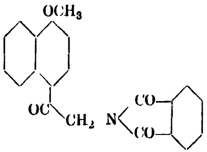
4-methoxy-ω-iodoacetonaphthone, prepared in the usual way, crystallised from alcohol as pale yellow prismatic needles M P 71°–73°

0 1242 gm of substance gave 0 0898 gm of AgI

Found I = 38 22%, $C_{13}H_{11}O_2I$ requires I = 38 90%

No pure products could be obtained from the above by the usual method of reaction with urotropine, and our plan to prepare the 4-methoxy-ω-aminoacetonaphthone in this way had therefore to be given up

4-methoxy-naphthacyl phthalimide



2 5 gms of 4-methoxy-ω-iodoacetonaphthone and 2 gms of potassium phthalimide (1·1 mol) in 15 c c alcohol were heated together for three hours under reflux, cooled in ice and treated with 5 c c water to dissolve the KI The product was filtered, washed with alcohol and water and crystallised from acetic acid White prismatic needles M P 216° Yield, 1·9 gms

0 1820 gm of substance gave 6 6 c c nitrogen at 31° and 739·3 mm pressure

Found · N = 3·95%, $C_{21}H_{15}O_4N$ requires N = 4·07%

4-hydroxy-ω-aminoacetonaphthone hydrobromide 1·2 gms of *p*-methoxy naphthacyl phthalimide were dissolved in boiling glacial acetic acid, 15 c c of concentrated hydrobromic acid added and the mixture heated under reflux for 4-5 hours with the exclusion of moisture It was then poured into 40 c c water, filtered from the separated phthalic acid and the filtrate evaporated to dryness on the water-bath The residue of impure *hydrobromide* of the base was crystallised twice from dilute hydrobromic acid Colourless needles M P 268°-270° (decomp)

0 1154 gm gave 4 8 c c nitrogen at 30 5° and 742 mm pressure; also 0·1500 gm gave 0·0983 gm AgBr

Found. N =4 57%, Br = 27 90%

$C_{12}H_{12}O_2NBr$ requires N = 4·96%, Br = 28·34%

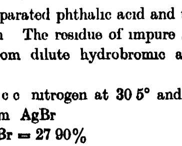
The picrate crystallised from water as yellow needles M P 186°-187° (decomp).

0 0680 gm gave 8 2 c c nitrogen at 31° and 741 mm pressure

Found N = 13 20%, $C_{18}H_{14}O_9N_4$ requires N = 13 03%

SYNTHESIS OF 1-PHENYL-3,4,DIHYDRO-4-KETO-7-METHOXY-5 6-BENZO-ISOQUINOLINE

Benzoyl-ω-amino-4-methoxy-acetonaphthone



A mixture of α-naphthol methyl ether (10 gms), carbon disulphide (40 c c), and anhydrous aluminium chloride (10 gms) was treated little by little with hippuryl chloride (12 6 gms) prepared by the method of Fischer (*Ber* , 1905, *38*, 612), and the mixture vigorously shaken with the complete exclusion of moisture It was then gently refluxed on the water bath for two hours and allowed to stand overnight. The supernatant layer of carbon disulphide was poured off, the residue washed once with 25 c c petroleum ether and the solid product thrown into crushed ice and acidified with an excess of concentrated HCl The separated solid was filtered, washed with dilute alkali and then with water several times, and finally crystallised from a mixture of alcohol and chloroform Long, colourless needles M P 151° Yield, 7 5 gms 4·5 gms of α-naphthol-methyl ether were recovered from the carbon disulphide and petroleum ether extracts

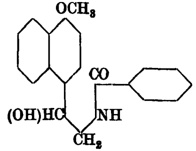
0 01482 gm gave 0 04076 gm CO_2 and 0·00747 gm H_2O, 0·1454 gm gave 6·2 c c nitrogen at 32° and 739 mm. pressure

Found C = 74·99%, H = 5 60%; N = 4·61%.

$C_{20}H_{17}O_3N$ requires C = 75·23%, H = 5·33%, N = 4 39%

Attempts to oxidise the product to 4,methoxy-naphthoic acid were unsuccessful

N-benzoyl-β-hydroxy-(4-methoxy-naphthyl-1)-ethyl amine



0 5 gm of 4-methoxy-benzoyl-ω-aminoacetonaphthone and a solution of 0 75 gm of sodium dissolved in 10 c c absolute methanol were boiled together with 1 gm of zinc dust for 3-4 hours on the water-bath The alcoholic solution was filtered hot and diluted with excess of water The carbinol which separated out as yellow flocks was dried and crystallised twice from a mixture of benzene and ligroin White leaflets M P 217°–219° (decomp)

0 01512 gm gave 0 04160 gm CO_2 and 0 00844 gm H_2O
Found C = 75·01%, H = 6·20%
$C_{20}H_{19}O_3N$ requires C = 74 76%, H = 5 92%

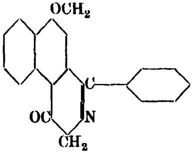
Attempted oxidation of 4-methoxy-benzoyl-ω-aminoacetonaphthone to 4-methoxy-naphthoic acid 0·5 gm substance suspended in 10 c c dilute NaOH (1N) was treated with 10 c c of 'Perhydrol' and allowed to stand overnight The original compound was recovered completely by filtration

Warming the substance with dilute HNO_3 resulted in resinification and hence no pure product could be isolated

1 gm of substance was treated with $KMnO_4$ in acetone drop by drop till there was a permanent pink colour on leaving for some time The solution was filtered and evaporated to dryness, the solid washed with water and crystallised from alcohol M P 151° This was only the original substance

Hydrolysis of 4-methoxy-benzoyl-ω-aminoacetonaphthone to 4-hydroxy-ω-amino-acetonaphthone hydrobromide The benzoyl-aminoacetonaphthone (1 gm) dissolved in boiling acetic acid was treated with 10 c c concentrated hydrobromic acid and the mixture heated under reflux for 4-5 hours It was then poured into 30 c c water, filtered and the solution concentrated when benzoic acid separated out The filtrate was evaporated to dryness on the water bath and the residual solid crystallised from dilute hydrobromic acid. Colourless needles. M P 268°–270° (decomp) This was identical with the sample obtained by hydrolysis of 4-methoxy naphthacyl phthalimide, there being no lowering of melting point on admixture. The picrates derived from the two samples were also found to be identical. (M.P. 186°-187°.)

1-phenyl-3,4-dihydro-4-keto-7-methoxy-5 6-benzoisoquinoline



1 gm of 4-methoxy-benzoyl-aminoacetonaphthone and 2 c c phosphorus oxychloride in 5 c c toluene were heated together under reflux for an hour on the sand-bath, moisture being excluded with a calcium chloride tube The slightly coloured solution was poured on to crushed ice, when a greyish yellow solid separated out The mixture was allowed to attain the room temperature and the solid material filtered, washed with water and then with petroleum and dried on the plate It crystallised from alcohol as colourless prismatic needles M P 101°-102° Yield, 0 7 gm The aqueous filtrate from the above did not yield any other basic substance on working up in the usual way

The benzo-isoquinoline dissolved easily in acetone, chloroform and ether, sparingly in alcohol, benzene or toluene and was insoluble in water or petroleum ether The solutions in these organic solvents were characterised by a fine blue fluorescence It was a weak base and did not dissolve in dilute acids even on warming It dissolved partly in hot concentrated acids but on dilution of the solution the base was not reprecipitated On rubbing with concentrated HCl in the presence of a little alcohol, a greenish-yellow solid was formed, which, after crystallisation from methanol, melted rather indefinitely between 145°-160° This was evidently the hydrochloride

0 01508 gm gave 0 04417 gm CO_2 and 0 00694 gm H_2O, also, 0 1040 gm gave 4 5 c c nitrogen at 32° and 741·4 mm pressure.

Found C = 79 89%, H = 5 12%; N = 4·72%

$C_{20}H_{15}O_2N$ requires C = 79 73%, H = 4 98%, N = 4 65%

The hydrobromide crystallised from absolute alcohol as greenish yellow needles M P 201°-203° (decomp)

0·1162 gm of substance gave 0 0574 gm. AgBr

Found Br = 20 01%, $C_{20}H_{16}O_2NBr$ requires Br = 20 93%

The methiodide. 0 5 gm of the substance in 3 c c chloroform and 1 c c methyl iodide were heated together in a sealed tube at 100° for an hour The separated dark green crystalline solid was filtered, washed with a little chloroform and finally recrystallised from alcohol Dark green, glistening needles M P. 195° (decomp).

0·1436 gm. of substance gave 0·0766 gm of AgI.

Found I = 28 82%; $C_{21}H_{18}O_2NI$ requires I = 28 67%

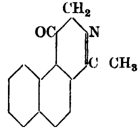
The picrate was rather easily obtained in a state of purity by mixing together the constituents in warm alcoholic solutions It crystallised from alcohol as slender golden yellow needles M P 158° (decomp)

0·1094 gm gave 10·6 c c nitrogen at 31° and 743·3 mm pressure

Found N = 10·64%, $C_{26}H_{18}O_9N_4$ requires N = 10·56%

The reduction of the keto-isoquinoline with zinc and sulphuric acid was tried but only unchanged material was recovered

Synthesis of 1-methyl-3,4,dihydro-4-keto-5 6-benzoisoquinoline



4 gms of acetyl-ω-amino-1-acetonaphthone (see p 161) and 8 c c of phosphorus oxychloride in 15 c c toluene were gently refluxed for an hour on the sand-bath, with the exclusion of moisture The slightly coloured solution was poured on to crushed ice and the mixture allowed to attain the room temperature when an almost clear solution resulted It was filtered from a little tarry matter and repeatedly extracted with chloroform The chloroform extract was washed with dilute alkali and water, dried over potassium carbonate and distilled The keto-isoquinoline was left behind as an oil (2·4 gms) The aqueous acid solution did not yield any other basic substance on working up in the usual way

0·02032 gm of the oil gave 0·06259 gm CO_2 and 0·00930 gm H_2O

Found C = 83·99%, H = 5·09%

$C_{14}H_{11}ON$ requires C = 84·41%, H = 5·53%

The methiodide crystallised from chloroform and alcohol as long colourless needles. M P 208°-209° (decomp)

0·1404 gm gave 0·0942 gm of AgCl

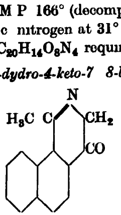
Found I = 36·17%, $C_{15}H_{14}ONI$ requires I = 36·18%

The picrate obtained in the usual way crystallised from acetic acid as yellow rosettes of needles M P 166° (decomp)

0·1070 gm gave 12·5 c c nitrogen at 31° and 743 mm pressure

Found. N = 12·82%, $C_{20}H_{14}O_8N_4$ requires N = 12·79%

Synthesis of 1-methyl-3,4,di-dydro-4-keto-7 8-benzoisoquinoline



2 gms of acetyl-ω-amino-2-acetonaphthone (see p 159) and 4 c c of phosphorus oxychloride in 10 c c toluene were gently refluxed for an hour on the sand-bath, with the exclusion of moisture The solution was poured on to crushed ice, the clear aqueous sloution exhausted with chloroform and the chloroform extract worked up as before 1 4 gms of a crystalline solid was left behind The keto isoquinoline crystallised from alcohol as long, colourless prismatic needles M P 90°-91° No other basic product was obtained on working up the acid solution in the usual way

0 01004 gm gave 0 03084 gm CO_2 and 0 00502 gm H_2O, also 0 0914 gm gave 5·8 c c nitrogen at 31° and 744 mm pressure

Found C = 83 79%, H = 5 56%, N = 6 97%

$C_{14}H_{11}ON$ requires C = 84 41%, H = 5 53%, N = 6 70%

The hydrobromide crystallised from dilute hydrobromic acid as clusters of colourless needles M P 251° (decomp)

0 1130 gm gave 0 095 gm AgBr

Found Br = 36 02%, $C_{14}H_{12}ONBr$ requires Br = 36 34%

The methiodide crystallised from absolute alcohol as dark red needles M P 158°-160° (decomp)

0 1060 gm gave 0 0707 gm of AgI

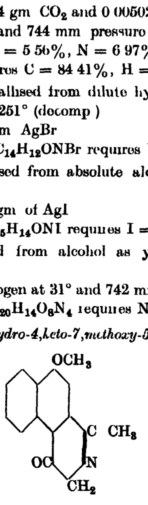
Found I = 35 90%, $C_{15}H_{14}ONI$ requires I = 36 18%

The picrate crystallised from alcohol as yellow needles M P 193° (decomp)

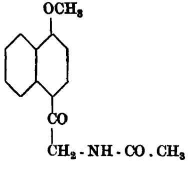
0 0704 gave 8·1 c c nitrogen at 31° and 742 mm pressure

Found N = 12 62%, $C_{20}H_{14}O_8N_4$ requires N = 12 78%

Synthesis of 1,methyl-3,4-dihydro-4,keto-7,methoxy-5 6,benzoisoquinoline



(a) *Preparation of 4,methoxy-acetyl-ω-amino-acetonaphthone*



Acetyl glycine was obtained by the method of Radenhauser (*J Prakt Chem*, 1895, *52*, 438), and the chloride prepared according to the directions given by Max (*Ann*, 1909, *369*, 286) 6 8 gms of the chloride were condensed with 7 gms of α-naphthol methyl ether in 30 c c carbon disulphide in the presence of 6 gms. of anhydrous aluminium chloride, and the product isolated in the usual manner The acetylaminoacetonaphthone crystallised from alcohol as colourless needles, M P 94°-95° Yield, 4 8 gms

0·1637 gm gave 8 2 c c N_2 at 26° and 752 mm

Found : N = 5 65%, $C_{15}H_{15}O_3N$ requires N, 5 45%

(*b*) *Preparation of the benzo-isoquinoline* The acetylaminoacetonaphthone (3 gms), toluene (10 c c) and phosphorus oxychloride (4 c c) were heated to boiling on a sand-bath for an hour and the product worked up as usual The isoquinoline crystallised from ligroin as colourless needles, M P 74° Yield, 2·3 gms

0 1908 gm gave 10 2 c c N_2 at 27° and 752 mm

Found N = 6 02%, $C_{15}H_{13}O_2N$ requires N, 5 81%

The hydrobromide crystallised in colourless prisms M P 217° (decomp)

0 2046 gm gave 0 1200 gm AgBr

Found Br = 24 96%, $C_{15}H_{14}O_2NBr$ requires Br, 24 91%

The methiodide separated from chloroform as stout red needles, M P 211°-213° (decomp)

0 1974 gm gave 0 1204 gm AgI

Found I = 32 97%

$C_{16}H_{16}O_2NI$ requires I, 33 32%

The *picrate* crystallised from alcohol as orange red prisms M P 164° (decomp)

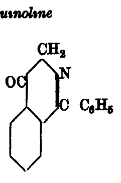
0 1420 gm gave 15 33 c c N_2 at 27° and 752 mm

Found: N = 12 06%

$C_{21}H_{16}O_9N_4$ requires N, 11 96%

Benzoyl-ω-amino-acetophenone was prepared from 15 gms of freshly prepared hippuryl chloride (cf Gabriel, *Ber*, 1910, *43*, 134, Pictet, *ibid*, 2387), 20 c c dry benzene and 12 gms of anhydrous aluminium chloride Colourless needles from dilute alcohol, M P 122°-123° Yield, 1 2 gms.

1,phenyl-3,4,dihydro-4,keto-isoquinoline



Benzoyl-ω-aminoacetophenone (1 gm), phosphoryl chloride (2 c c) and toluene (5 c c) were gently refluxed on the sand-bath for 45 minutes, and the isoquinoline was isolated in the usual way Colourless needles from alcohol, M P 70° Yield, 0 8 gms

0 1302 gm gave 7 0 c c N_2 and 753 mm

Found N = 6 06%

$C_{15}H_{11}ON$ requires N, 6 33%

The picrate crystallised from water as yellow needles M P 173° (decomp)

0 1228 gm gave 13 3 c c N_2 at 27° and 753 mm

Found N = 12·20%

$C_{21}H_{14}O_8N_4$ requires N, 12 44%

2-methoxy-benzoyl-ω-aminoacetonaphthone was prepared in a very poor yield (0 25 gm) from 10 gms of β-naphthyl methyl ether, 12 6 gms of hippuryl chloride and 10 gms of aluminium chloride in 30 c c of carbon disulphide It crystallised from alcohol as glistening rectangular plates M P 167°-168° Considerable amounts of unreacted nerolin and of hippuric acid were isolated from the reaction mixture

0 1563 gm gave 5 8 c c N_2 at 26° and 752 mm

Found N = 4 20%

$C_{20}H_{17}O_3N$ requires N, 4 39%

4-methoxy benzoyl-ω-aminoacetophenone was prepared in the same way from 15 gms hippuryl chloride, 10 6 gms anisol and 12 gms aluminium chloride in 25 c c CS_2 Colourless rectangular plates M P 112°-113° The yield was only 0 5 gm

0 1776 gm gave 7 7 c c N_2 at 26° and 752 mm

Found N = 5 10%

$C_{16}H_{15}O_3N$ requires N, 5·21%

Attempts to cyclise these ketones to the isoquinolines have not hitherto been successful

SUMMARY

The action of the common cyclising agents like phosphoryl chloride on the acetyl derivatives of 2,methoxy- and 4,methoxy-naphthyl-methyl amine and of 4,methoxy-naphthyl-α-methyl-methylamine has been investigated Only non-basic materials, difficult to purify, were obtained The expectation that the Bischler-Napieralsky reaction could be applied to these acet-α-naphthyl methyl amides so as to get benzoisoquinolines by condensation at the peri-position has, therefore, not been realised The failure to cyclise these compounds is parallel to the fruitless attempts made by other workers to prepare isoquinolines from bases of the benzyl-amine type

Attempts made to prepare substituted naphthyl-β-ethyl-amines from easily accessible naphthalene compounds and to cyclise them to benzoisoquinolines have also not been successful

A simple practical method for the preparation of the acyl-ω-amino-acetophenones and -acetonaphthones, sometimes in good yields, by the condensation of phenol- and naphthol-ethers with hippuryl and acetyl glycyl chlorides has been worked out Several of these compounds have been converted by the usual methods into 3,4,dihydro-4,keto-benzo-isoquinolines, moderately good yields being obtained

The benzo-isoquinolones prepared in this manner are found to be rather weak bases It has not been possible yet to reduce them to the corresponding tetrahydro-isoquinolines

PRESIDENCY COLLEGE,
MADRAS,
27th November, 1939

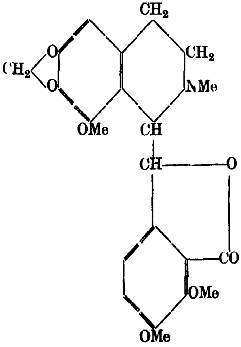
STUDIES IN THE ISOQUINOLINE SERIES

PART V 4,COUMARO-METHYL, 3,COUMARO-METHYL, AND 3,COUMARYL-1-ISOQUINOLINES

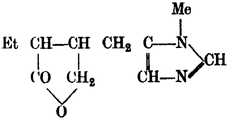
By B B DEY *and* K SANKARAN

(*Read January 2, 1940*)

Although the lactone ring has been found to occur so frequently in nature, either as α- or γ-pyrones, in glucosides and in natural colouring matters, there are only a few instances known of the presence of such ring systems in heterocyclic bases The two best known examples of natural alkaloids containing the lactone ring are those of narcotine and pilocarpine, having respectively the following constitutions —



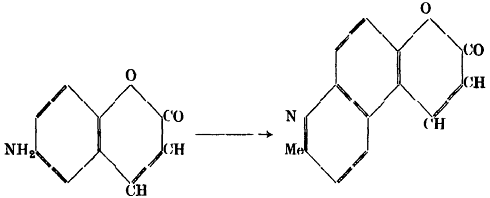
Narcotine



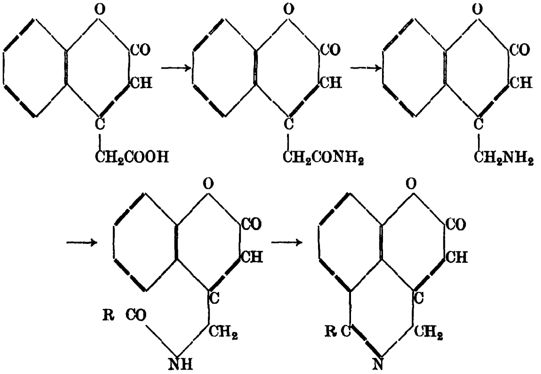
Pilocarpine

Among the laboratory attempts at syntheses of compounds, containing the combined lactone and heterocyclic basic group, may be mentioned the work of Dey and Goswami (*J Chem Soc* , 1919, *15*, 531), on 1 8-ψ-isonaphthoxazones by the application of Skraup's reaction to 6-amino coumarins, and its extension to homologues of quinolino-6 5-α-pyrones, by the application of the Doebner-Miller reaction to these 6-amino-coumarins (Dey and Seshadri, *J I C S* , 1926, *Vol III*, p. 187), thus.

VOL. VI—No. 2. [Published July 20th, 1940.



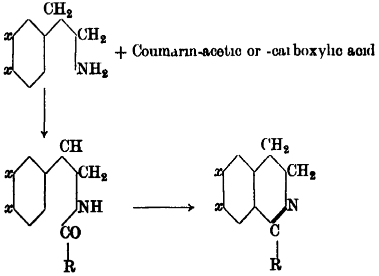
It was hoped in the beginning that isoquinolino-pyrones, like the quinolino-pyrones mentioned above, might be synthesised on similar lines by the route shown below —



This expectation has unfortunately not been realised by us, all attempts at obtaining the 4-coumaryl methyl amine from the corresponding coumarin-4-acetamide being unsuccessful

Isoquinolines with a coumaryl group substituted in position 1 were, however, readily obtained from the coumarin-4- and 3-acetic acids, and β-phenyl ethyl amines like homopiperonyl and homoveratryl amines The reactivity and properties of these coumarin acids (Dey and co-workers, *J I C S*, 1924, *Vol I*, 107, *ibid*, 1931, *Vol VIII*, 247; *ibid*, 1931, *Vol VIII*, 817, *ibid*, 1934, *Vol XI*, 381) have been found to be quite similar to those of acetic and phenyl acetic acids The substitution of these for the usual fatty or aromatic acids in the syntheses of 1-substituted isoquinolines, and a study of the changes in physiological properties, if any, resulting from the inclusion of the pyrone ring in their molecules, seemed, therefore, to be of considerable importance The recent patents of E Merck & Co [D R P 613 005 (1935), E Merck & Co, Dalmer and Werder, 612 592 (1937) reference in American Chemical Abstracts, (1937, November)] wherein have been prepared the coumarin 3-carboxylic acid salts of papaverine and of trans-ephedrine, which are claimed to have well-marked sedative and antispasmodic action, lent additional interest to the investigation Merck's preparations were only salts of the isoquinoline bases with the coumarin carboxylic acids No syntheses of coumaryl isoquinolines are known and it was therefore considered desirable to undertake a systematic study of the syntheses, properties and possible pharmacological actions of these bodies

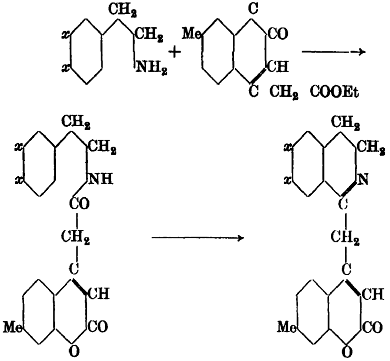
The syntheses of the 1-coumaryl isoquinolines via the β-phenyl ethyl amides of the coumarin acids and cyclisation of the latter into the isoquinolines by the Bischler-Napieralsky method has been found to proceed normally and smoothly according to the following scheme —



where R = a coumaro-4-methyl or a coumaryl-group This reaction furnishes a general method of synthesis of 1-coumaryl isoquinolines

The formation of isoquinolines from homopiperonylamine and homoveratryl amine on the one hand and (a) 7-methyl coumarin 4-acetic acid, (b) coumarin 3-carboxylic acid, and (c) coumarin 3-acetic acid on the other is shown in the schemes A, B and C given below —

'*A*'


CH2
CH2
NH2
x
x
+
C
Me
CO
CH
C CH2 COOEt
NH
CO
CH2
C
CH
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Me
O
N
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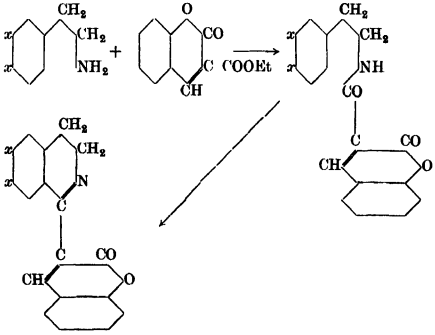
CH2
C
CH
CO
Me
O

'*B*'


CH2
CH2
NH2
x
x
+
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CO
C COOEt
CH
NH
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CH
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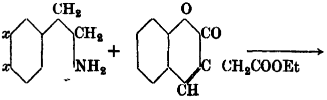
'*C*'


CH2
CH2
NH2
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x
+
O
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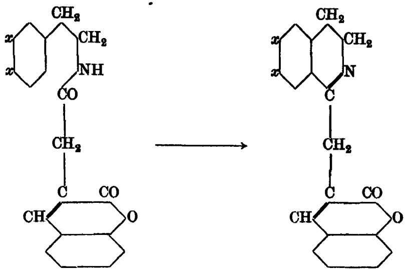
C CH2COOEt
CH



Isoquinolines from coumarin-4,acetic acids 1, (7-methyl-4-coumaro methyl)-6 7,methylene dioxy- or dimethoxy-3 4,dihydro-isoquinoline and derivatives

7-methyl coumarin 4-acetic acid was prepared by the direct method of Dey and Row (*J I C S*, 1924, *Vol I*, 107) from citric acid and meta-cresol Homopiperonylamine was prepared by the method of Buck and Perkin (*J Chem Soc*, 1924, *125*, 1675) and homoveratryl amine by a slightly modified method of Ray (*J I C S*, 1927, Vol IV 403) The condensation of these to the intermediary amides was effected generally by heating the amine and the ethyl ester (Fries and Volk, *Ann*, 1911, *379*, 107) at 120°, in solvents like toluene or xylene The difficulty arising from the tendency of the coumarin-4-acetic acid to be decarboxylated was thus avoided The amides separated in an almost pure condition and the yields were generally good Cyclisation occurred readily when phosphorus oxychloride was used as the cyclising agent, and the major portion of the reaction product was obtained as the hydrochloride of the base While the free bases are yellow, the hydrochlorides are colourless crystalline solids They have a bitter taste The isoquinolines are not strong bases and are readily precipitated from aqueous solutions of their hydrochlorides by sodium carbonate solution Reduction to the tetrahydro isoquinolines has been accomplished in most cases, using zinc and sulphuric acid The hydrochloride of the tetrahydro base from homoveratryl amine and 7-methyl coumarin 4-acetic acid ester has been found to decompose rather rapidly when kept

Isoquinolines from coumarin-3,carboxylic acids 1, (3-coumaryl)-6 · 7,methylene dioxy- or dimethoxy-3 4,dihydro-isoquinolines and derivatives

The coumarin-3,carboxylic ethyl ester required in these investigations has been prepared in almost quantitative yields by the method of Knoevenagel (*Ber*, *31*, 2593) from salicyl aldehyde and malonic ester. The condensation to the intermediary amides was carried out according to the method described in Section A Both the free base and its hydrochloride have been obtained in satisfactory yields under the usual conditions of experimentation The interesting fact was noticed that the free bases in this case were colourless and their hydrochlorides were yellow while the opposite is the case with the compounds described in Section A A curious observation to record is that relating to the physical character of the cyclisation product of the amide derived from homoveratryl amine It invariably set itself to a beautiful fluorescent jelly, which dissolved in hot water, but again formed the jelly on cooling In this case, the hydrochlorides were obtained by passing dry HCl into benzene solutions of the respective bases Reduction of the 1, (3-coumaryl)-6 7 methylene dioxy-3 4, dihydro-isoquinoline was not successful

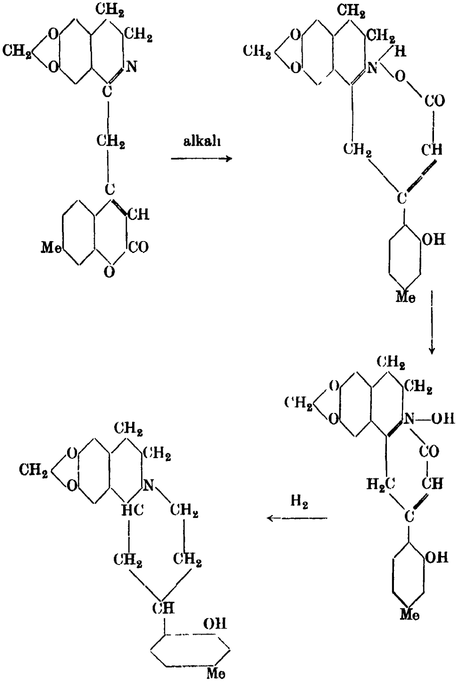
Isoquinolines from coumarin-3,acetic acids 1, (3 coumaro-methyl)-6 7,methylene dioxy- or dimethoxy-3 4-dihydro-isoquinolines and derivatives

The coumarin-3, acetic acid was prepared by the method of Dey and Sankaranarayanan (*J I C S*, 1931, *Vol VIII*, 817) The condensation to the amide was effected by heating the two components without any solvent The yields were not as satisfactory as in the former cases, large amounts of by-products being obtained Cyclisation, too, led to the formation of considerable amounts of tarry products which made it rather difficult to isolate the pure isoquinoline The free base is yellow in colour but the salt which was first obtained as a solid soon turned into an oil which was only partly soluble in water, showing that partial decomposition had taken place.

General properties of the coumaryl-isoquinolines

All the five 1-coumaryl isoquinolines which have been synthesised have a weak basic character They dissolve in acids only slowly and can be completely extracted from their acid solutions with chloroform Salts such as the hydrochloride, hydrobromide, nitrate and picrate have, however, been prepared in the pure state The methiodides were generally obtained pure on heating the base and methyl iodide under pressure They begin to decompose on attempting to crystallise them from water or alcohol The bases, too, decomposed slowly on keeping and were found to be preserved best in the form of their hydrochlorides

A study of the action of alkali on these bodies should be of interest, as compounds of the pyridocoline type are expected to arise as a result of the opening of the pyrone ring The following scheme explains the reactions involved.—



Investigations in this direction are in progress

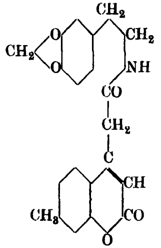
EXPERIMENTAL

The homopiperonylamine required in these investigations was prepared mainly by the method of Buck and Perkin (*J Chem Soc*, 1925, *125*, 1675)

7,methylcoumarin-4-acetic acid was prepared by the method of Dey and Row (*J I C S*, 1924, *Vol I*, 197) 9 g of the coumarin acetic acid crystallising in needles, M P 190°, and 4 g of 4,7-dimethyl coumarin, M P 134°, were obtained from 24 g of citric acid and 10 g. of metal-cresol.

The ethyl ester (Fries and Volk, *Ann*, 1911, *379*, 107) was easily prepared by saturating an absolute alcoholic solution of the acid with dry HCl gas

7-methyl, coumarin-4,acet-3 4-methylene dioxy-β-phenyl ethyl amide



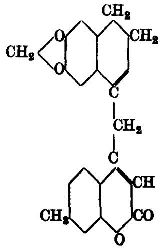
3 30 g of homopiperonylamine and 4 90 g of the ester were heated together with 30 c c of toluene for a period of 3 to 4 hours at its boiling point, moisture being excluded On cooling, the amide separated out as a crystalline solid which was filtered, washed with dilute HCl and water alternately, and crystallised from a large quantity of alcohol Clusters of snow-white needles M P 197° Yield, 4 5 g

0 2482 g gave 8 4 c c. of nitrogen at 29° and 764 mm

Found N, 3 77 per cent.

$C_{21}H_{19}O_5N$ requires N, 3 83 per cent

1-(7,methyl-4,coumaromethyl)-6 7,methylene dioxy-3 4,dihydro-isoquinoline



2 g of the above amide were dissolved in 20 c c toluene and refluxed on the sand-bath with 12 c.c. of phosphorus oxychloride for 1½ hours The contents became dark coloured and a crystalline solid appeared towards the

end of the reaction, the quantity of which increased as the flask cooled down The deeply coloured fluorescent solution was poured into crushed ice The thick oil which separated, solidified in about an hour It was filtered, washed with dilute alcohol and finally crystallised from hot water Shining plates, M P 265° (d) Yield, 0 9 g This was found to be the hydrochloride of the base

The coloured acid filtrate was separated from the toluene layer and then repeatedly exhausted with chloroform and the extract dried over anhydrous potassium carbonate On removing the solvent, the free base was left behind as a coloured mass which crystallised from benzene or from toluene-petroleum ether mixture in short stout needles, M P 184° Yield, 0 5 g

0 1696 g of the base gave 0 4514 g of CO_2 and 0 0770 g of water, 2 609 milligrams gave 0 090 c c of nitrogen at 22 5° and 767 mm pressure, 9 276 milligrams of the hydrochloride gave 3 420 milligrams of AgCl

Found C, 72 69 per cent, H, 5 04 per cent, N, 4 02 per cent

$C_{21}H_{17}O_4N$ requires C, 72 60 per cent, H, 4 89 per cent, N, 4 03 per cent

Found Cl, 9 11 per cent

$C_{21}H_{17}O_4NCl$ requires Cl, 9 25 per cent

(Analyses by Dr Ing A Scholler of Berlin)

The free base is yellow in colour and is soluble in all common organic solvents It can be easily extracted from acid solutions The aqueous solution of the hydrochloride is strongly fluorescent and is extremely bitter to the taste The free base is precipitated from aqueous solutions of the hydrochloride by sodium carbonate solution, both the free base and the hydrochloride decompose slowly on keeping

The hydrobromide was obtained as fern-shaped crystals when the free base was rubbed with a few drops of concentrated hydrobromic acid, M P 268° (d)

0 186 g gave 0 0800 g of AgBr.

Found. Br, 18 53 per cent

$C_{21}H_{18}O_4NBr$ requires Br, 18 69 per cent

The methiodide was obtained by heating the base and methyl iodide in a sealed tube and washing the dark coloured solid product with a little chloroform Attempts at crystallisation failed as the compound began to decompose M P 228° (d)

0·1415 g. gave 0·0675 g of AgI

Found: I, 25·79 per cent

$C_{22}H_{20}O_4NI$ requires I, 25 97 per cent

The nitrate was obtained as plates by rubbing the base with dilute nitric acid M P 156°

The picrate was obtained as a yellow precipitate on mixing alcoholic solutions of the base and picric acid, it crystallised from glacial acetic acid as yellow needles M P. 248° (d)

0 1790 g gave 15 6 c c of nitrogen at 28° and 762 7 mm
Found N, 9 73 per cent
$C_{27}H_{20}O_{11}N_4$ requires N, 9 72 per cent

1,(7,methyl-4,coumaromethyl)-6,7,methylenedioxy-1,2,3,4-tetrahydro-isoquinoline

1 g of the dihydro-base, 3 g of zinc dust and 0 05 g of copper sulphate were mixed with 30 c c of water and warmed on the water-bath 2 5 c c of concentrated sulphuric acid was added during the course of an hour and the mixture was shaken well so that hydrogen was evolved only slowly As the reaction progressed the yellow solution became gradually colourless It was filtered after an hour, cooled, basified with sodium carbonate solution and then exhaustively extracted with chloroform and the extract dried over anhydrous potassium carbonate Removal of this left the tetrahydro compound as an oil Yield, 0 3 g

The hydrochloride was obtained as plates by rubbing this oil with a few drops of concentrated hydrochloric acid M P 214° (d) The tetrahydro base was precipitated as a solid by basifying the hydrochloride solution with sodium carbonate M P 175° (decomp)

0·1386 g of the base gave 5 1 c c of nitrogen at 29° and 759 5 mm
Found. N, 4 15 per cent
$C_{21}H_{19}O_4N$ requires N, 4·01 per cent

0 1935 g of the hydrochloride gave 0·0745 g of AgCl
Found. Cl = 9 50 per cent
$C_{21}H_{20}O_4NCl$ requires Cl, 9 20 per cent

The picrate was obtained as a yellow precipitate from the aqueous solution of the hydrochloride by the addition of a saturated solution of picric acid It crystallised from acetic acid as rhombic plates M P 207° (d)

0 1556 g gave 13·4 c c of nitrogen at 30° and 764·5 mm
Found· N, 9 56 per cent
$C_{27}H_{22}O_{11}N_4$ requires N, 9 68 per cent

The acetyl derivative was prepared by treating the tetrahydro base with a few drops of acetic anhydride and crystallising the product from dilute alcohol M P 204° (d)

0·0694 g. gave 2 2 c c of nitrogen at 30° and 767·6 mm
Found. N, 3·53 per cent
$C_{23}H_{21}O_5N$ requires N, 3 58 per cent

Homoveratrylamine was prepared by the method of Buck and Perkin modified by Ray (*J I C S* , 1927, *Vol IV*, 403) The yields at each stage were excellent.

7,methyl-4-coumarin acet-3 4-dimethoxy-β-phenyl-ethyl amide

1·8 g of the ester and 2·45 g of homoveratrylamine were heated under reflux in xylene solution for 3 hours. On cooling, the amide separated out as a crystalline solid It was washed with dilute HCl, and crystallised from alcohol Short rods, M P 174° Yield, 2 6 g

0 0931 g gave 3 c c nitrogen at 31° and 762 5 mm

Found N, 3 63 per cent

$C_{22}H_{23}O_5N$ requires N, 3 67 per cent

1, (7,methyl-4,coumaro-methyl)-6,7-dimethoxy-3,4-dihydro-isoquinoline

The above amide (2 g) was dissolved in 16 c c toluene and gently refluxed on the sand-bath with 11 c c of phosphoryl chloride for an hour and a half, the solution which had originally a straw yellow colour acquired a deep reddish tint On pouring the reaction mixture into ice water, a thick oil separated which solidified after about an hour, this was collected, washed with water and then with the minimum amount of chloroform and crystallised from hot water The ***hydrochloride*** separated as thin rhombic crystals M P 108° Yield, 0 6 g The toluene layer was carefully removed from the filtrate and extracted five times with chloroform (10 c c) and the extract dried over anhydrous potassium carbonate After removal of the solvent the isoquinoline remained as an oil which rapidly solidified It crystallised from a mixture of toluene and petroleum ether as short stout needles M P 181° Yield, 0 5 g The base is yellow in colour and dissolves readily in the common organic solvents The hydrochloride is colourless and its aqueous solution has a mild green fluorescence It affords the rare example of a base melting higher than its salt

0 1238 g of the base gave 4 45 c c nitrogen at 30° and 764 mm

Found N, 3 98 per cent

$C_{22}H_{21}O_4N$ requires N, 3·85 per cent

0 1035 g of the hydrochloride gave 0 0374 g of AgCl

Found Cl, 8 94 per cent

$C_{22}H_{22}O_4NCl$ requires Cl, 8 88 per cent

The hydrobromide was readily obtained as colourless crystals on mixing the base with aqueous hydrobromic acid M P 207° (d)

0·1423 g gave 961 g of AgBr

Found Br, 18 24 per cent

$C_{22}H_{22}O_4NBr$ requires Br, 18·02 per cent

The methiodide was formed on heating the free base with excess of MeI in a stoppered bottle at 100° M P 182° (d).

0·1201 g gave ·056 g. of silver iodide.

Found: I, 25 22 per cent.

$C_{23}H_{24}O_4NI$ requires I, 25·15 per cent

The picrate separated from glacial acetic acid as beautiful straw yellow prisms.

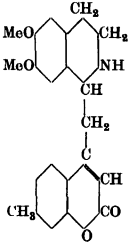
0·1904 g gave 16·1 c c nitrogen at 30·3° and 759·8 mm

4

Found N, 9 32 per cent

$C_{28}H_{24}O_{11}N_4$ requires N, 9 46 per cent

Reduction to the 1,2,3,4-tetrahydro-isoquinoline



2 g of the hydrochloride of the dihydro base was dissolved in the minimum amount of water and heated on the boiling water-bath with a tiny crystal of copper sulphate and 6 g of zinc dust for 3 hours 5 c c of concentrated sulphuric acid was then slowly added during the course of an hour when the solution became practically colourless It was filtered, cooled, basified with sodium carbonate solution and extracted repeatedly with chloroform The tetrahydro-base was obtained as an oil Yield, 0·5 g The *hydrochloride* separated as crystals on adding a few drops of concentrated hydrochloric acid to the oily base M P 98° The salt is found to decompose on keeping

0 1129 g of the base gave 4·25 c c. of nitrogen at 30° and 764 mm

Found N, 4 16 per cent

$C_{22}H_{23}O_4N$ requires N, 3 83 per cent

0 2166 g of the hydrochloride gave 0 0723 g. of AgCl

Found Cl, 8 25 per cent

$C_{22}H_{24}O_4NCl$ requires Cl, 8 80 per cent

The picrate melted at 165°

0·2389 g gave 19 30 c c nitrogen at 26·8° and 766 6 mm

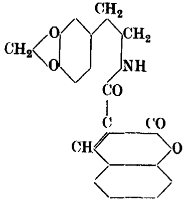
Found N, 9 12 per cent

$C_{28}H_{26}O_{11}N_4$ requires N, 9·42 per cent

1-(3,coumaryl)-6 · 7-methylene dioxy-3 4-dihydro-isoquinoline

Coumarin 3-carboxylic ester, prepared by Knoevenagel's method (*Ber*, *31*, 2593) from salicyl aldehyde (3 g), malonic ester (4 5 g) and a few drops of piperdine, crystallises from alcohol as elongated plates M P 94° Yield, 3·5 g.

1-(3 coumaryl)-3 4, methylene dioxy-β-phenyl ethyl amide

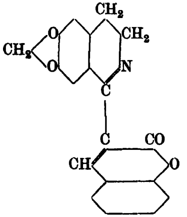


4 36 g of the ester, 3 30 g of homopiperonyl amine and 30 c c of toluene were heated to boiling for 3 to 4 hours, and the separating solid purified in the usual way Snow-white needles (from alcohol) M P 214° Yield, 4 8 g 0 2116 g gave 7 8 c c of nitrogen at 31° and 747 7 mm

Found N, 4·07 per cent

$C_{19}H_{15}O_5N$ requires N, 4 10 per cent

1, (3-coumaryl)-6 7-methylene dioxy-3 4-dihydro isoquinoline



2 g. of the amide suspended in 25 c c toluene was refluxed on the sand-bath with 12 c c. of phosphorus oxychloride for an hour and a half The solution acquired a dark brown colour and a small amount of yellow crystals separated out towards the end of the reaction The contents were poured into ice water, the yellow solid filtered and the filtrate repeatedly extracted with chloroform On distilling off the dried solvent the isoquinoline was left behind as a coloured solid which was crystallised from benzene Fern-shaped crystals M P 253° (d) The yellow solid that had separated was found to be the impure hydrochloride It was dissolved in hot water and basified, when the free base was liberated as a colourless solid Total yield of the base, 1 4 g

0·1676 g. of the base gave 6 9 c c of nitrogen at 30° and 766 3 mm

Found. N, 4·58 per cent

$C_{19}H_{13}O_4N$ requires N, 4 38 per cent

The hydrochloride was prepared by passing dry HCl gas into a dry benzene solution of the base M P 221° (d)

0·1895 g gave 0 0773 g. of AgCl
Found · Cl, 10·08 per cent
$C_{19}H_{14}O_4NCl$ requires Cl, 10·09 per cent

The hydrobromide obtained in the usual way melted at 214° (d)

0 2225 g gave 0·1037 g of AgBr
Found Br, 19 84 per cent
$C_{19}H_{14}O_4NBr$ requires Br, 20 00 per cent

The methiodide was obtained by heating the components in a sealed tube M P 218° (d)

0 1201 g gave 0 0620 g of AgI
Found I, 27 8 per cent
$C_{20}H_{16}O_4NI$ requires I, 27 6 per cent

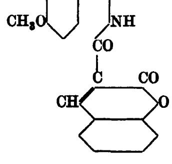
The picrate crystallised from acetic acid as stout yellow prisms M P 213° (d)

0 1236 g gave 11 6 c c nitrogen at 32° and 766 2 mm
Found · N, 10·30 per cent
$C_{25}H_{16}O_{11}N_4$ requires N, 10·21 per cent

Reduction to the 1,2,3,4-tetrahydro-isoquinoline 2 5 g of the dihydro base was dissolved in the minimum amount of dilute sulphuric acid and refluxed on the boiling water-bath with 7 g of zinc dust and a small crystal of copper sulphate, and a few c c of concentrated sulphuric acid added during the course of the reduction (about one hour) The colourless solution was filtered hot, cooled and basified with sodium carbonate and extracted with chloroform On evaporating the dried solution the base was left behind as an oil Yield, 0·9 g

The hydrochloride, prepared by rubbing the above oil with a few drops of concentrated HCl, melted indefinitely between 196° and 205°.

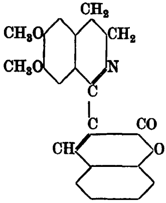
1, (3 coumaryl)-3 4-dimethoxy-β-phenyl ethyl amide



3·62 g of homoveratryl amine and 4 36 g of the ester boiled in toluene (20 c.c) gave nearly 4 g. of the amide, crystallising from alcohol in prisms M.P 158°

0 1347 g gave 4 96 c c of nitrogen at 31° and 758 3 mm
Found N, 4 03 per cent
$C_{20}H_{19}O_5N$ requires N, 3 96 per cent

1, (3, coumaryl)-6 7-dimethoxy-3 4-dihydro-isoquinoline



3 g of the amide, suspended in 20 c c toluene and 22 c c of phosphorus oxychloride were gently refluxed on the sand-bath for 2 hours The jelly-like mass which separated on pouring the solution into water was found to be the hydrochloride of the base It was collected, washed and redissolved in boiling water On allowing the clear filtrate to cool, the whole of it set to a light fluorescent jelly again The hot aqueous solution of the jelly was basified, when the isoquinoline separated as a yellowish white solid which crystallised from benzene in short needles M P 194°. Yield, 1 8 g

0·1263 g gave 4·45 c c. nitrogen at 31° and 761 5 mm.
Found N, 3 93 per cent
$C_{20}H_{17}C_4N$ requires N, 4 17 per cent

The hydrochloride was obtained as a canary yellow powder on passing dry hydrochloric acid gas into a dry benzene solution of the base M.P 204° (d.).

0 1025 g. gave 0·0489 g of AgCl.
Found: Cl, 9 45 per cent
$C_{20}H_{18}O_4NCl$ requires Cl, 9 55 per cent

The hydrobromide, obtained in a similar manner, melted at 212° (d.)

0·1587 g. gave 0·450 g. of AgBr.
Found : Br, 19 12 per cent
$C_{20}H_{18}O_4NBr$ requires Br, 19 23 per cent.

The picrate was obtained as a yellow precipitate by mixing alcoholic solutions of the free base and picric acid It crystallised from glacial acetic acid as golden yellow needles M P 238° (d)

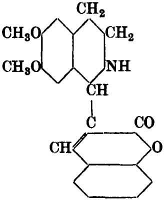
0 1433 g gave 13 2 c c of nitrogen at 31° and 760 mm

Found N, 10 20 per cent

$C_{26}H_{20}O_{11}N_4$ requires N, 9 93 per cent

The methiodide melted at 204° (d)

1, (3-coumaryl)-6 7 dimethoxy-1 2 3 4-tetrahydro-isoquinoline



1 g of the dihydro base, 3 g of zinc dust and 20 c c of water were heated on the boiling water-bath and 3 c c of concentrated sulphuric acid was added during the course of about 3 hours The solution, which became colourless when reduction was complete, was filtered, cooled and basified with sodium carbonate solution The whole was repeatedly exhausted with chloroform, and on removal of the dried solvent the tetrahydro compound was left as an oil This was rubbed with a few drops of concentrated hydrochloric acid when the hydrochloride separated as a crystalline powder M P 248° Yield, 0 6 g On basifying the aqueous solution of the hydrochloride the free base was obtained as shining plates M.P 187°

0 1754 g of the base gave 6·77 c c nitrogen at 30° and 762 4 mm

Found N, 4 30 per cent

$C_{20}H_{19}O_4N$ requires N, 4·16 per cent

0 1025 g of the hydrochloride gave 0 0380 g of AgCl

Found Cl, 9 17 per cent

$C_{20}H_{20}O_4NCl$ requires Cl, 9 50 per cent.

The picrate obtained in the usual way melted at 228° (d)

0·2154 g gave 19 5 c c. of nitrogen at 29 5° and 761 25 mm.

Found N, 9 96 per-cent

$C_{26}H_{22}O_{11}N_4$ requires N, 9·89 per cent

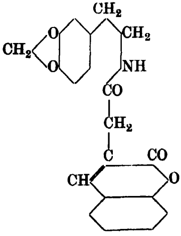
Synthesis of 1, (3,coumaro-methyl)-6 7-methylene dioxy-3 4-dihydro-isoquinoline

(*a*) *Preparation of coumarin-3, acetic acid* Salicylaldehyde (6 g), sodium succinate dried at 130° for several hours (11 g) and freshly prepared succinic anhydride (14 g) were heated in a flask fitted with an air-condenser at 170°–180° for 4 hours The yellow crystalline mass was transferred on cooling to a mortar with the aid of small amounts of hot water and triturated well with a cold solution of sodium bicarbonate (30 g in 60 c c water) The major portion of the solid dissolved with effervescence and after standing for an hour, the solution was filtered from the insoluble residue of 3,3′-dicoumaryl (M P 250°–260°)

The clear filtrate was acidified with dilute HCl and allowed to stand overnight when clusters of beautiful pale yellow plates (2 4 g) were found to have separated M P 154°-155° A single crystallisation from boiling absolute alcohol with the addition of animal charcoal gave shining colourless plates, M P 158° Yield, 1 8 g

The ethyl ester was prepared by suspending the acid in absolute alcohol and saturating with dry hydrochloric acid gas until a clear solution was obtained, and then leaving for 12 hours Colourless needles, M P 88°

(*b*) *Preparation of (coumarin 3-acet)-3 4 methylene dioxy-β-phenyl ethyl amide*



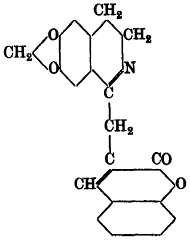
4 72 g. of ethyl ester of the acid and 4 g of the amine were heated for a period of 3 hours in the oil-bath at 160°–170°, moisture being excluded The cold mass was washed with dilute alcohol and acid and finally crystallised from alcohol. Colourles needles, M P 202° Yield, 3 g (1 3 g of homopiperonyl amine was recovered)

0·1028 g gave 3·4 c c. of nitrogen at 28° and 765 mm

Found N, 3·70 per cent

$C_{20}H_{17}O_5N$ requires N, 3 98 per cent.

1, (3 coumaro methyl)-6 7-methylene dioxy-3 4-dihydro-isoquinoline



A mixture of 3 g of the amide, 15 c c of toluene and 16 c c of phosphorus oxychloride was refluxed on the sand-bath for an hour and a half On pouring into ice water, the major portion of the reaction product separated as a dark oil The whole was extracted with chloroform, the extract dried over anhydrous potassium carbonate, and the chloroform removed on the water-bath The oily residue was treated with warm dilute HCl, filtered and basified with sodium carbonate The process was repeated twice when a clean solid was obtained This crystallised from a mixture of benzene and petroleum ether as thin plates M P 175° (d)

0 1386 g gave 5 10 c c nitrogen at 29° and 759 5 mm

Found N, 4 15 per cent

$C_{20}H_{15}O_4N$ requires N, 4 20 per cent

The hydrochloride On adding a few drops of concentrated HCl to a suspension of the base in water, it at first turned oily but on keeping overnight in contact with acid, the hydrochloride separated as colourless, stout needles M P 224°

0 1552 g gave 0·0604 g AgCl

Found Cl, 9·61 per cent

$C_{20}H_{16}O_4NCl$ requires Cl, 9 63 per cent

The methiodide was prepared by heating the base and methyl iodide in a sealed tube M P 225° (d)

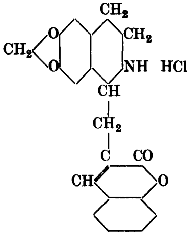
The picrate crystallised from glacial acetic acid as clusters of short needles M P 213°

0 1904 g. gave 16 1 c.c of nitrogen at 30 3° and 759·8 mm

Found N, 9·62 per cent.

$C_{26}H_{18}O_{11}N_4$ requires N, 9·96 per cent.

1, (3,coumaro-methyl)-6 7,methylene dioxy-1 2 3 4,tetrahydro-isoquinoline



The dihydro base (2 g), zinc dust (6 g) and a crystal of copper sulphate were heated with 40 c c water on the boiling water-bath and 6 c c concentrated sulphuric acid added during the course of three hours The unreacted zinc was removed and the filtrate cooled, basified with sodium carbonate solution, and completely extracted with chloroform On removal of the dried solvent the tetrahydro compound remained as an oil Yield, 0 9 g

The hydrochloride separated as thin plates on the addition of a few drops of concentrated HCl to the oil M P 245° (d) The free base was obtained as a solid on basifying the aqueous solution of the hydrochloride M P 110°

0 1536 g of the hydrochloride gave 0 0582 g of AgCl

Found Cl, 9 38 per cent

$C_{20}H_{18}O_4NCl$ requires Cl, 9 56 per cent

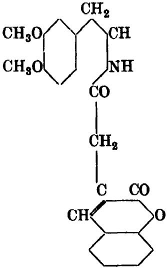
The picrate obtained in the usual way crystallised from dilute acetic acid as plates M P 187° (d)

0 1593 g gave 14 6 c c of nitrogen at 30° and 748 mm

Found N, 10 18 per cent

$C_{26}H_{20}O_{11}N_4$ requires N, 9 93 per cent

Condensation of homo-veratryl amine and coumarin-3,acetic ester. Coumarin-3,acet-3 : 4 dimethoxy-β-phenyl ethyl amide.



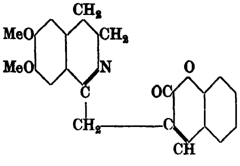
1.81 g. of the homoveratryl amine and 2.36 g. of coumarin 3 ethyl acetate were heated together in an oil-bath at 160°–170° for a period of 4 hours, moisture being excluded. On cooling, the homogeneous semi-solid mass was dissolved in the minimum amount of hot alcohol and filtered. The amide separated from the cold solution as clusters of needles which were recrystallised from alcohol. M.P. 212°. Yield, 2 g. (0.5 g. of the amine hydrochloride was recovered.)

0.1478 g. gave 5.6 c.c. of nitrogen at 31.5° and 762 mm.

Found: N, 4.06 per cent.

$C_{21}H_{21}O_5N$ requires N, 3.82 per cent.

1-(3, coumaro-methyl)-6, 7-dimethoxy-3, 4-dihydro-isoquinoline.



The amide (3 g.), phosphoryl chloride (22 c.c.) and toluene (20 c.c.) were refluxed for 2 hours on the sand-bath and then poured into excess of ice-water. The hydrochloride of the base separated out. It was washed and crystallised from hot water. Short colourless prisms which do not melt even at 360°. The filtrate was exhaustively extracted with chloroform. The extract dried and distilled The base was left behind as a reddish solid It crystallised from benzene and petroleum ether as orange yellow rhombic plates M P 222° (d) On rubbing this with a few drops of hydrochloric acid, the colourless hydrochloride melting above 360° was obtained

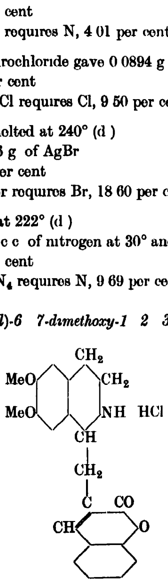
0 1990 gm of the base gave 7 c c of nitrogen at 30° and 750 3 mm
Found N, 3 91 per cent
$C_{21}H_{19}O_4N$ requires N, 4 01 per cent

0 2312 g of the hydrochloride gave 0 0894 g of AgCl
Found Cl, 9 21 per cent
$C_{21}H_{20}O_4NCl$ requires Cl, 9 50 per cent

The hydrobromide melted at 240° (d)
0 116 g gave 0 0486 g of AgBr
Found Br, 18 52 per cent
$C_{21}H_{20}O_4NBr$ requires Br, 18 60 per cent

The picrate melted at 222° (d)
0 2334 g gave 20 1 c c of nitrogen at 30° and 748 mm
Found N, 9 55 per cent
$C_{27}H_{22}O_{21}N_4$ requires N, 9 69 per cent

1, (3,coumaro-methyl)-6 7-dimethoxy-1 2 3 4-tetrahydro-isoquinoline.



The dihydro-isoquinoline (1 g), zinc dust (3 g) and a small crystal of copper sulphate were heated with water (30 c c) on the boiling water-bath and 2 5 c c. of concentrated sulphuric acid were added during the course of 2 to 3 hours The colourless solution was filtered from excess of zinc and the filtrate cooled and basified with sodium carbonate solution Extraction with chloroform, drying the extract and evaporating the solvent gave the tetrahydro compound as an oil It was converted into the solid hydrochloride by rubbing with strong HCl This crystallised from hot water as colourless plates M P. 236° (d).

0 0778 g of the hydrochloride gave 0 0280 g of AgCl

Found Cl, 8 91 per cent

$C_{21}H_{22}O_4NCl$ requires Cl, 9 16 per cent

SUMMARY

1,coumaryl-isoquinolines have been synthesised from homopiperonyl and homoveratryl amines and coumarin-4, and 3,acetic esters and coumarin 3-carboxylic esters, by the Bischler-Napieralsky method

These dihydro-isoquinolines are feeble bases of a yellow colour, the salts being colourless The tetrahydro-isoquinolines are stronger bases and are colourless

PRESIDENCY COLLEGE,
MADRAS,
27th November, 1939

STUDIES IN THE ISOQUINOLINE SERIES

PART VI 2′ AND 4′,QUINOLYL-*l*-ISOQUINOLINES

By MISS B S ALAMELA *and* B B DEY

(*Read January 2, 1940*)

A survey of recent literature on the subject of isoquinolines brings into prominence two interesting lines of development in this field In the first place, the syntheses of these bases have been carried out under physiological conditions, i e conditions approximating to those existing in nature (cf Spath and Kreuts, *Monatsch*, 1928, *50*, 341, Späth and Berger, *Ber* , 1930, *63*, 2098, Schöpf and Bayerle, *Ann* , 1934, *513*, 190, Hahn and Schales, *Ber* , 1935, *68*, 24, etc), the results contributing to a clearer understanding of the phytochemical mechanism of the formation of alkaloids containing this ring system in plants, and secondly, new types of isoquinolines have been synthesized with a view to press them into service in the treatment of amoebic dysentery, malaria and other diseases The realization particularly of the magnitude and complexity of the malaria problem has led in recent years to the inauguration of a series of important investigations having for their object the syntheses of chemical specifics, mostly derivatives of quinolines and acridines but a few belonging to the isoquinoline group as well, and a study of their antimalarial, amoebicidal and other possible therapeutic properties [Barger and Robinson, *Journ Chem Soc London, 1929*, 2947, 2952, 2959, 2965, Kermack and co-workers, *ibid* , *1930*, 1356, *1931*, 3089, 3096, *1935*, 1143, 1421, Ray and co workers, *ibid* , *1931*, 976, *J Indian Chem Soc* , 1932, *9*, 215 , 1933, *10*, 197, *J Amer Chem Soc* , 1932, *54*, 3988, *J pr Chem* , 1933, ii, *136*, 117, Robinson and co-workers, *Journ Chem Soc London, 1933*, 1467, *ibid* , *1934*, 1264, 1267, 1322, 1520, 1524, Magidson and co-workers, *J Gen Chem Russ* , 1934, *4*, 1047, *Arch Pharm* , 1935, *273*, 320, Kritschevski and Meerson, *J Immunitat*, 1933, *79*, 180, 438, Mietzsch and Mauss, *Angew Chem* , 1934, *47*, 633, Fieldman and Kopeliovitzsch, *Arch Pharm* , 1935, *273*, 488, Goodall and Kermack, *Journ. Chem Soc London, 1936*, 1546, Berkenheim, *J Gen Chem Russ* , 1936, *6*, 1039, 1043, Basu and Das-Gupta, *J Indian Chem Soc* , 1937, *14*, 468, Child and Pyman, *Journ Chem Soc London, 1931*, 36]

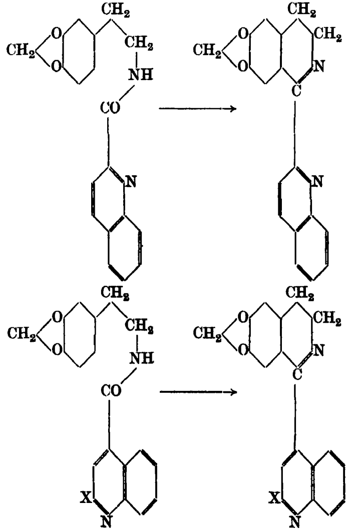
While the cinchona alkaloids still retain their undoubted pre-eminence in this field, recent work has brought to light many important facts concerning their true values and also their limitations, and synthetic drugs like Plasmoquin and Atebrin appear to have proved their superiority to the natural alkaloids in the treatment of certain special types of malaria Attention has thus been drawn to the possibilities of employing different types of 1, substituted isoquinolines in the treatment of various kinds of malarial infections and with this end in view, heterocyclic acids like picolinic and nicotinic acids have been

VOL. VI—No. 2. **[Published July 26th, 1940**

condensed with β-phenyl ethyl amines for the synthesis of isoquinolines with a pyridine ring in 1, position (Clemo, McIlwain and McG Morgan, *J C S*, 1936, 610, Sugasawa and Kuriyagawa, *Ber*, 1936, *69* [B], 2068)

In pursuance of the systematic studies in the isoquinoline series which have been undertaken in this laboratory, attempts have now been made with success to link two new heterocyclic ring systems, viz (*a*) quinoline, and (*b*) benzo-α-pyrone, to carbon atom 1 in the isoquinoline ring The quinolyl-isoquinolines form the subject matter of the present investigation The coumaryl isoquinolines have been described in Part V of this series

The condensation of quinaldinic and of 2,methyl- and 2,phenyl-cinchoninic acids with homopiperonylamine resulted in the formation in good yields of the respective amides which underwent smooth cyclization to the corresponding 3,4,dihydro-isoquinolines as explained in the following scheme —



The quinolyl-isoquinolines are well-defined bases which are colourless but which form deep yellow salts with mineral acids While the 2,quinolyl-isoquinolines function as monacid bases yielding stable monohydrochlorides, the 4,quinolyl derivatives are found to be diacidic and form, in accordance with expectation, stable dihydrochlorides The preparation of analogous isoquinolines with other heterocyclic substituents and of their reduction products is in progress

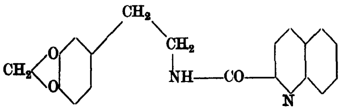
EXPERIMENTAL

Quinaldinic acid was prepared both by the method of Besthorn and Ibele (*Ber.*, 1906, *39*, 2329) from quinaldine and formalin and by the method of Reissert (*Ber* , 1905, *38*, 1603) from quinoline, benzoyl chloride, and potassium cyanide The former method was preferred on account of the simplicity of the process and the better yield of the product

The methyl ester was prepared according to the direction given by Hammick (*Journ Chem Soc* , 1923, p 2883) 5 4 g of methyl quinaldinate crystallizing from ligroin in long needles, M P 86°, were obtained from 6 g of the acid

Homopiperonylamine was prepared in the usual way by the method of Buck and Perkin (*J Chem Soc* , 1924, *125*, 1693) 10 g of the pure amino, B P 162°/22 mm were obtained starting from 20 g of piperonal Attempts were made to prepare the amine by the electrolytic reduction process from piperonylidene nitromethane but none of them were very successful, only poor yields of the amine being obtained at the end

α,quinolinoyl-β-3,4,methylene dioxy-phenyl ethylamide



This was prepared by the following three methods —

(*a*) Powdered quinaldinic acid (1 73 g) was heated with homopiperonylamine (1 65 g) at 160°-170° on an oil-bath for five hours The oily reaction product was triturated with alcohol when it solidified and the solid residue was finally crystallized twice from alcohol (norit-charcoal) Yield, 0·5 g of amide M P. 110°

(*b*) Quinaldinic acid (1 g) was covered with dry chloroform (50 c c), thionyl chloride (1 g) added, and the mixture refluxed on the steam bath for three hours After removing the chloroform and excess of thionyl chloride under reduced pressure, dry benzene (10 c.c) and homopiperonylamine (0 92 g) were successively added, the mixture heated on a steam bath for an hour and the product treated with crushed ice, basified with ammonia, extracted thrice with benzene and the benzene extract dried over potassium carbonate On distilling off the benzene, a reddish oil was left behind which solidified on rubbing with alcohol. Crystallization from alcohol gave thin plates M P 110°. Yield, 0·7 g The alcoholic mother liquor, on dilution with water, gave a further 0 5 g of the slightly impure amide

(c) Methyl quinaldinate (1 85 g) and homopiperonylamine (1 65 g) were heated on the steam-bath for three hours Crystallization of the reaction product from alcohol (norit) gave colourless glistening plates M P 110° Yield, 2 6–2 7 gms

The third method proved to be the most satisfactory and was employed for preparing larger quantities of the amide

23 04 mg of the substance gave 60 75 mg of CO_2 and 10 86 mg of H_2O, 26 08 mg gave 2 055 c c of nitrogen at 33° and 763 mm

Found C, 71 91, H, 5 24, N, 8 83 per cent

$C_{19}H_{16}O_3N_2$ requires C, 71 22, H, 5 037, N, 8 75 per cent

The *hydrochloride* of the α,quinolinoyl, β-phenyl ethylamide was prepared by passing dry HCl gas into a suspension of the amide (0·5 g) in dry benzene (20 c c) It crystallized from absolute alcohol in dark yellow prisms M P 167°

60 19 mg required 8 2 c c of 1 043 N/50 NaOH

Found Cl, 10 08 per cent

$C_{19}H_{16}O_3N_2$ HCl requires Cl, 9 94 per cent

The hydrochloride is very easily hydrolyzed even in the presence of moisture

The *picrate*, obtained by mixing alcoholic solutions of the amide and picric acid, crystallized in fibrous needles M P 115°

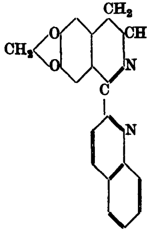
The picrate was dried in vacuum at room temperature 42 44 mg gave 4 752 c c of nitrogen at 33° and 765 mm

Found N, 12 58 per cent

$C_{19}H_{16}O_3N_2$ $C_6H_3O_7N_3$ requires N, 12 72 per cent

Attempts to prepare the *methiodide* by the usual method were not successful, the unchanged amide being recovered at the end

1-2′-α,quinolyl-6,7,methylene dioxy-3,4,dihydro-isoquinoline



The above amide (2 g), phosphorus oxychloride (6 c c) and dry toluene (12 c c) were heated on an oil-bath at 120°–130° for three hours A thick oil separated out which solidified to a hard gummy mass on cooling Petroleum ether was added to the mixture until there was no further turbidity, the clear liquid poured off and the residue washed with petroleum ether and finally treated with water (150 c c) containing 1 c c strong HCl The acid aqueous extract was shaken once with ether to remove any toluene, strongly cooled and basified with strong ammonia After standing for three hours, the dirty white solid was collected and crystallized from alcohol (norit) The isoquinoline separated in bundles of colourless rectangular plates M P 118° Yield, 1 4 g

It dissolves in cold dilute acids with a deep yellow colour which changes to deep red on addition of more acid The acid solution, on dilution, showed a pale blue fluorescence

18 01 mg gave 49 46 mg CO_2 and 7 97 mg H_2O, and 18 22 mg of the base gave 1 472 c c of nitrogen at 33° and 760 mm

Found C, 74 89, H, 4 92, N, 9 02 per cent

$C_{19}H_{14}O_2N_2$ requires C, 75 44, H, 4 67, N, 9 27 per cent

29 9 mg of the base (dried in vacuum), dissolved in 405 mg of camphor, depressed the melting point by 10°

Found M W , 295 3

$C_{19}H_{14}O_2N_2$ requires M W , 302

The *platinichloride* was prepared in the usual way Orange yellow crystals M P 210°.

0 10415 mg (dried at 110°/5 mm) gave 01999 g Pt

Found Pt, 19 20 per cent

$[C_{19}H_{14}O_2N_2]_2$ H_2PtCl_6 requires Pt, 19 23 per cent

The *hydrochloride* was prepared by passing dry HCl gas into a solution of the base (0 5 g) in benzene (8 c c), rubbing the deep red sticky solid with a little absolute alcohol and then crystallizing from the same solvent Clusters of yellow needles M P. 241°

0 17007 g requires 18 1 c c of 0 555 N/20 caustic soda

Found Cl, 10 47 per cent.

$C_{19}H_{14}O_2N_2$ HCl requires Cl, 10 49 per cent

The base appears therefore to be mono-acidic

The *picrate* was prepared by mixing alcoholic solutions, crystallized in prisms M.P. 210°

7 65 mg of the picrate gave 0 84 c c of N_2 at 764 75 mm. and 27°C.

Found. N, 12 63 per cent

$C_{19}H_{14}O_2N_2$ $C_6H_3O_7N_3$ requires N, 13·18 per cent.

The *methiodide* was prepared by heating the components in a closed bottle at 100° for four hours, washing the sticky product with alcohol and finally crystallizing it from alcohol or water Long rectangular plates M P. 245°

0 09225 g gave 0 04441 g AgI

Found I, 26 0 per cent

$C_{19}H_{14}O_2N_2$ CH_3I requires I, 28 6 per cent

The reduction of the dihydro base with zinc and sulphuric acid or with tin and hydrochloric acid could not be effected satisfactorily Catalytic reduction with palladized—norit was ultimately found to be the most successful method

A solution of 0 5 g of the base in 10 c c of glacial acetic acid containing 0 2 g of the catalyst in suspension was shaken in an atmosphere of hydrogen until there was no more absorption of gas The catalyst was filtered and the colourless solution diluted and basified with ammonia The white precipitate was filtered and crystallized from alcohol It melted at 160° Yield, 0 4 g

The tetrahydro base was dried in vacuum at 30° 18 12 mg gave 49 66 mg of CO_2 and 8·98 mg. of water.

Found. C, 74 73, H, 5 51 per cent

$C_{19}H_{16}O_2N_2$ requires C, 74 98, H, 5 30 per cent

The *platinichloride*, prepared in the usual way, melted to a clear red liquid at 204°

0 1167 g of the double salt gave 0 0221 g of Pt

Found Pt, 18 93 per cent

$[C_{19}H_{16}O_2N_2]_2$ H_2PtCl_6 requires Pt, 19 16 per cent

The *hydrochloride*, which was hygroscopic, melted at 142°

0 1231 g of the hydrochloride dried in vacuum required 13 55 c c of 1 292 N/50 sodium hydroxide solution

Found Cl, 10 08 per cent

$C_{19}H_{16}O_2N_2$ HCl requires Cl, 10·41 per cent

The *picrate*, crystallized from dilute alcohol, melted to a thick liquid at 96°–98°

22·64 mg gave 2 618 c c. of nitrogen at 33° and 758 mm

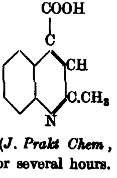
Found N, 12 87 per cent

$C_{19}H_{16}O_2N_2$ $C_6H_3O_7N_3$ requires N, 13 13 per cent

The reduced base is therefore mono-acidic

Syntheses of 4′,quinolyl-1-isoquinolines.

α,Methyl-cinchoninic acid,

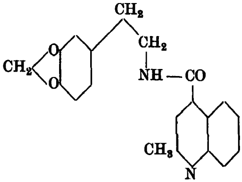


This was prepared by the method of Pfitzinger (*J. Prakt Chem*, 1897, *56*, 284) by refluxing isatin with acetone and alkali for several hours. Nearly

16 g of the cinchoninic acid crystallizing from boiling water in needles, M P. 241°, were obtained from 15 g of isatin.

The *methyl ester* of 2,methyl-cinchoninic acid crystallized from ligroin in colourless needles M P 60°-61°

α,methyl-γ,quinolinoyl-β-3 4-methylene dioxy-phenyl ethylamide



A mixture of the methyl ester of cinchoninic acid (2 g) and homopiperonylamine (1 6 g) was heated at 100° for five hours The reaction product was a gum which solidified on rubbing with alcohol Crystallization from 50 per cent alcohol gave the amide as colourless thin plates M P 153° (after drying). Yield, 1 8–1 9 g The amide is a strong base dissolving readily in cold dilute acids (The *hydrochloride* was prepared by saturating a benzene solution of the amide with HCl gas It crystallized from absolute alcohol as pale yellow scales M P 194°)

22 30 mg of the amide gave 58 69 mg of CO_2 and 11 30 mg of H_2O. 16 61 mg gave 1 148 c c of nitrogen at 33° and 762 mm

Found C, 71 78, H, 5·63, N, 8 10 per cent

$C_{20}H_{18}O_3N_2$ requires C, 71 83, H, 5 43, N, 8 38 per cent

0 20497 g of the hydrochloride required 22 55 c c of 1 291 N/50 caustic soda

Found Cl, 10 07 per cent

$C_{20}H_{18}O_3N_2$ HCl requires Cl, 9·57 per cent

The *picrate* crystallized from dilute alcohol as small plates M P 190°.

16 69 mg gave 1·84 c c. of nitrogen at 31° and 761 mm

Found N, 12 28 per cent

$C_{20}H_{18}O_3N_2 . C_6H_3O_7N_3$ requires N, 12 43 per cent.

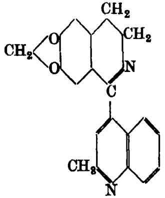
The *methiodide* was prepared by heating the components in a closed bottle for five hours on a steam bath It crystallized from alcohol in clusters of yellow plates M.P. 197°

0·18216 g gave 0·08433 g AgI

Found: I, 25·02 per cent

$C_{21}H_{21}O_3N_2I$ requires I, 26·65 per cent.

α,methyl-quinolyl-γ,6 7,methylenedioxy-3,4,dihydro-isoquinoline



The γ-quinolinoyl-phenyl ethylamide (1 g), phosphorus oxychloride (3 5 c c) and dry toluene (10 c c) were refluxed for three hours on an oil-bath at 120°-130° On cooling, 20 c c petroleum ether was added and after standing for an hour the clear supernatant liquid was decanted off and the gummy residue ground with 50 c c water containing 1 c c HCl After shaking the deep red aqueous acid extract with ether to remove any non-basic impurities and traces of toluene the solution was cooled in ice and basified with ammonia The granular solid was collected and crystallized from 50 per cent alcohol (norit) The base separated in glistening, colourless, rectangular plates M P 114° Yield, 0 8 gm

The isoquinoline is a strong base dissolving instantly in cold dilute acids and giving crystalline precipitates with Meyer's reagent and with potassium dichromate solution

17 38 mg gave 48 10 mg of CO_2 and 8 29 mg of H_2O 22 32 mg gave 1 758 c c of N_2 at 34° and 761 mm

Found C, 75 48, H, 5 30, N, 8 73 per cent.

$C_{20}H_{16}O_2N_2$ requires C, 75 91, H, 5 10, N, 8 86 per cent

The *platinichloride*, prepared in the usual way, decomposes gradually without melting, above 250°

0 06959 g dried at 110°, gave 0 01836 g platinum

Found Pt, 26 37 per cent

$C_{20}H_{16}O_2N_2$ H_2PtCl_6 requires Pt, 26 8 per cent

It behaves therefore as a diacidic base

The *hydrochloride*, prepared from a benzene solution of the base and dry HCl gas, separated from alcohol as orange yellow crystals M P 234° (decomp)

0·10140 g required 21 c c. of 1·291 N/50 caustic soda

Found Cl, 18 95 per cent

$C_{20}H_{18}O_2N_2Cl_2$ requires Cl, 18·23 per cent.

The *methiodide*, prepared in the usual way, crystallized from absolute alcohol as rectangular prisms M P 254° (decomp).

15 83 mg gave 31 85 mg of CO_2 and 5 98 mg of water

11307 g of substance dried at 100°, gave 05248 g AgI

Found C, 54 87, H, 4 20, I, 25 08 per cent

$C_{20}H_{16}O_2N_2$ CH_3I requires C, 55 01, H, 4 18, I, 27 7 per cent

The base therefore forms a mono-methiodide

The *picrate* crystallized from a small quantity of alcohol melting at 221° (decomp)

24 26 mg gave 3 083 c c of N_2 at 33 5° and 762 mm

Found N, 14·20 per cent

$C_{20}H_{16}O_2N_2$ $2C_6H_3O_7N_3$ requires N, 14 46 per cent

Reduction with zinc and sulphuric acid

The dihydro base (1 g) and zinc spangles (3 g) in water (30 c c) containing copper sulphate (0 05 g) was warmed on the water-bath (50°-60°) with the gradual addition of concentrated sulphuric acid in the course of two hours The orange yellow solution became colourless in about 20 minutes The excess of zinc was filtered off and the filtrate with the washings was cooled and basified with ammonia The white precipitate was filtered, dried and extracted with hot benzene The pale yellow oil (0 8 g), after removing the solvent, solidified on rubbing with a few drops of alcohol Crystallized from dilute alcohol, the tetrahydro base separated in colourless rhombic plates melting at 81°

17 40 mg gave 48 06 mg of CO_2 and 9 02 mg of water

Found C, 75 32, H, 5 76 per cent

$C_{20}H_{18}O_2N_2$ requires C, 75 56, H, 5 70 per cent

The *hydrochloride*, crystallized from absolute alcohol, melted at 275°

0 1054 g required 23 8 c c of 1 108 N/50 sodium hydroxide solution

Found. Cl, 17 72 per cent

$C_{20}H_{18}O_2N_2$ 2HCl required Cl, 18 18 per cent

The *picrate* separated from alcohol, melting at 202° 12 71 mg gave 1 62 c c of N_2 measured at 33° and 759 mm

Found. N, 14 21 per cent

$C_{20}H_{18}O_2N_2$ $2C_6H_3O_7N_3$ requires N, 14 42 per cent

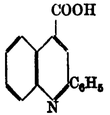
The *benzoyl derivative* crystallized from acetone-alcohol mixture and melted at 226°

20·27 mg. gave 1·146 c.c. of N_2 at 33° and 764 mm

Found N, 6·38 per cent

$C_{27}H_{22}O_3N_2$ requires N, 6 63 per cent

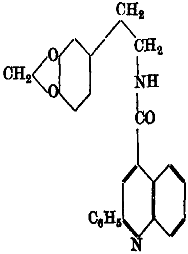
α,phenyl-cinchoninic acid,



This was prepared by the method of Pfitzinger (*loc cit*, p 292) 5·2 g of pale brown needles, M.P 208°-209°, were obtained from 5 g of isatin

The *methyl ester* was prepared by refluxing with methyl alcohol and sulphuric acid for three hours, basifying the diluted product with sodium carbonate and extracting with ether. It crystallized from ligroin in colourless needles M P 61° Yield, 4·7 g. from 5 g of the acid Claus and Brandt (*A.*, 1894, *252*, 106) previously obtained this ester by the process of heating the silver salt with methyl iodide in a sealed tube at 100°

α,phenyl-γ,quinolinoyl-β-3 4,methylene dioxy-phenyl ethylamide



The methyl ester (4·8 g) and homopiperonyl amine (3·0 g.) were heated for ten hours on the steam-bath The amide began to separate out after five hours. On cooling, the hard brown mass was powdered and washed with small amounts of ether The white residue was dried and crystallized from excess of boiling alcohol in which it was sparingly soluble Colourless rectangular plates M.P 185°

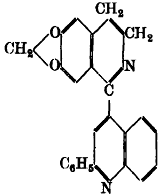
17 76 mg. gave 49·13 mg CO_2 and 8 51 mg H_2O 18·56 mg gave 1 167 c.c. of nitrogen measured at 763·9 mm and 33°

Found C, 75 44, H, 5·32, N, 7 05 per cent.

$C_{25}H_{20}O_3N_2$ requires C, 75 71, H, 5·09; N, 7·07 per cent

The amide behaved as a very feeble base and was quite insoluble in acids. Attempts to prepare the hydrochloride, picrate and methiodide were unsuccessful, only unchanged materials being recovered. This is obviously to be explained by the acidic influence of the phenyl group in 2, position in the quinoline ring.

α,phenyl-quinolyl-γ,1-6 7-methylene dioxy-3,4,dihydro-isoquinoline



The amide (1 85 g.) was refluxed with phosphorus oxychloride (10 c c) in boiling toluene (15 c c) for three hours at 130°-140° The reaction mixture was cooled, diluted with petroleum ether and allowed to stand for one hour and the clear supernatant liquid decanted off The red gummy residue was taken up in water (40-50 c c) containing a few drops of hydrochloric acid and the deep red aqueous solution extracted with ether to remove traces of toluene and any non-basic matter The ether-free solution was cooled strongly and basified with liquor ammonia The dihydro-isoquinoline which separated as a white powder was collected and crystallized from dilute alcohol It separated slowly in short rectangular plates, melting at 167° Yield, 1 5 g

It dissolves like the other two bases of this group readily in cold dilute acids with a characteristic yellow colour which changes to deep red with excess of acid The base exhibits a feeble greenish fluorescence in dilute acid solutions.

23 53 mg of the base gave 68 36 mg of CO_2 and 10 48 mg of H_2O 21 74 mg gave 1 472 c c of N_2 at 34° and 761 mm

Found C, 79 21, H, 4·95, N, 7·53 per cent

$C_{25}H_{18}O_2N_2$ requires C, 79 34, H, 4 80, N, 7 41 per cent

The *platinichloride* was obtained as a canary yellow precipitate which did not melt but decomposed above 290°

0·24933 g gave, on ignition, 0 06057 g of Pt

Found Pt, 24 30 per cent.

$C_{25}H_{18}O_2N_2$ H_2PtCl_6 requires Pt, 24 77 per cent

The *hydrochloride* separated from absolute alcohol in golden yellow flakes, M P 205° It is extremely hygroscopic.

0 3307 g. of the salt required 64·10 c c. of 1 108 N/50 sodium hydroxide solution.

Found Cl, 15 23 per cent.

$C_{25}H_{18}O_2N_2$ 2HCl requires Cl, 15 71 per cent

The base is diacidic in its platinum salt and its hydrochloride.

The *picrate* crystallized from acetone-alcohol mixture in hard prisms, melting at 211° (decomp.).

23·73 mg gave 2 332 c c of N_2 at 32° and 759 mm

Found N, 10 99 per cent

$C_{25}H_{18}O_2N_2$ $C_6H_3O_7N_3$ requires N, 11 53 per cent

The *methiodide* separated from absolute alcohol in yellow needles M P 286° (decomp.)

16 17 mg of the methiodide gave 35 32 mg of CO_2 and 6 14 mg of H_2O

0 0923 g. gave 04066 g of AgI

Found C, 59 58, H, 4 22, I, 23 8 per cent

$C_{25}H_{18}O_2N_2$ CH_3I requires C, 59 99, H, 4 07, I, 24 4 per cent

The base is monoacidic in its picrate and methiodide

Reduction with zinc and sulphuric acid

The dihydro base (1 g) and zinc spangles (3 g) were suspended in water (30 c c) containing copper sulphate (0 05 g) The mixture was kept warm at 50°–60° and concentrated sulphuric acid (2 5 c c) gradually added in the course of two hours The deep orange yellow solution became almost colourless in 20 minutes It was allowed to remain at 60° for a further half hour and filtered hot from the excess of zinc The filtrate together with the washings was cooled, basified with liquor ammonia and the precipitate collected and dried in vacuum The dry residue containing inorganic material was extracted with ether or hot benzene A pale yellow oil which solidified to a crisp solid was obtained Crystallized from ether, the tetrahydro base separated in brittle flakes melting at 92°–94°, with softening at 82°.

16 05 mg gave 46 25 mg of CO_2 and 7 81 mg of water

Found. C, 78 59, H, 5 41 per cent

$C_{25}H_{20}O_2N_2$ requires C, 78·93, H, 5 30 per cent

The *hydrochloride*, which is hygroscopic, sintered at 200° and melted completely to a clear liquid at 225°

0 1033 g requires 17 6 c c of 0 6348 N/25 sodium hydroxide solution.

Found: Cl, 15·34 per cent

$C_{25}H_{20}O_2N_2$ 2HCl requires Cl, 15 64 per cent

The *picrate*, prepared in the usual way, crystallized from dilute acetone in irregular plates, melting at 200°.

21·79 mg of the picrate gave 2·193 c c of N_2 at 34° and 759 mm

Found N, 11 19 per cent

$C_{25}H_{20}O_2N_2$ $C_6H_3O_7N_3$ requires N, 11·49 per cent

SUMMARY

A new series of isoquinolines with a quinoline ring attached to C-atom 1 in the isoquinoline ring have been synthesized They are colourless, crystalline bases which form deep yellow salts with mineral acids, picric acid, and methyl iodide The α,quinolyl-isoquinoline is exclusively monoacidic, whereas the

γ-quinolyl-isoquinolines are diacidic in their salts with mineral acids A study of the therapeutic properties of these and other similar compounds under investigation is in progress

PRESIDENCY COLLEGE,
MADRAS,
27th November, 1939

STUDIES IN THE ISOQUINOLINE SERIES

PART VII CYCLOHEXYL-METHYL ISOQUINOLINES

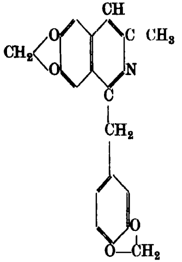
By B B DEY *and* P R VENKATARAMAN

(*Read January 2, 1940*)

Papaverine has been largely used as an antispasmodic Owing to the restrictions placed by the state on the manufacture of morphine, it appeared at one time that the amount of papaverine available from natural sources for meeting clinical demands would be inadequate Accordingly various synthetic products have been placed on the market for clinical use which have a close resemblance to papaverine in constitution and pharmacological action

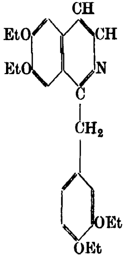
The following are some of the most important antispasmodics which have been placed on the market —

(1) Eupapaverine



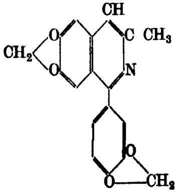
British Patent, 348956
Chem Zentr, *102*, *II*, 1196 (1931)

(2) Perparin



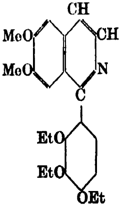
French Patent, 719638
Chem Zentr, *103*, *II*, 740 (1932)

(3) Neupaverine



German Patent, 613005

(4) Octaverine



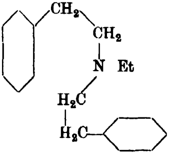
French Patent, 760825

VOL. VI—No. 2. [Published July 29th, 1940.

(5) 3,keto-4, benzoyl-3,4-dihydrobenzoxazine-1 4 British Patent, 370350 (*British Chem Abstracts*, B , 1932, 786)

(6) Syntropan The tropic acid ester of 3-diethylamino-2,2-dimethyl propanol-1 Fromherz, *Arch Exptl Path Pharmakol* , 1933, *173*, 86

(7) Ethyldi-β-phenyl-ethylamine
U S Patent, 2006114



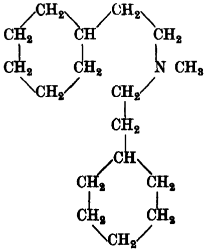
(8) Octin—the acid tartrate or hydrochloride of N, 1,5,trimethyl hexenyl-4,amine German Patent, 617536

(9) Transentin—diphenyl acetic acid ester of β-diethylamino-ethanol Meier, *Klin Wochschr* , 1936, *15*, 1403

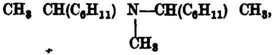
(10) Jwendal—tributyl acetamide (*Arch Exptl Pathol Pharmakol* , 1937, *186*, 552)

(11) Sestron—the hydrochloride of ethyldi-γ-phenyl-propylamine Kulz and Rosenmund, *Klin Wochschr* , 1938, *17*, 345

Recently, Blicke and Monroe (*J Amer Chem Soc* , 1939, *61*, 91) have synthesized methyldi-β-cyclohexyl-ethylamines which have proved to be strong antispasmodics They may be formulated thus .



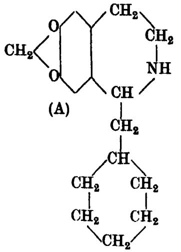
Although these compounds are obviously different from papaverine, they still bear an interesting relation to the completely hydrogenated papaverine molecule with the isoquinoline ring ruptured Blicke and Zienty (*ibid* , p. 93) have synthesized methyldi-α-cyclohexyl-ethylamine,

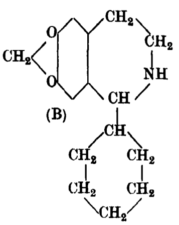


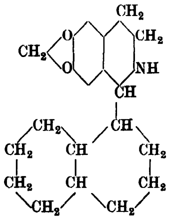
$$CH_3\ CH(C_6H_{11})\ \underset{CH_3}{\underset{|}{N}}—CH(C_6H_{11})\ CH_3,$$

which also shows equally strong antispasmodic properties

In the light of these experiments, it was hoped that polymethylene compounds substituted in position 1 of the 1,2,3,4-tetrahydro-isoquinolines should prove to be strong antispasmodics Accordingly, syntheses of the types of compounds A, B, and C, shown below, were undertaken

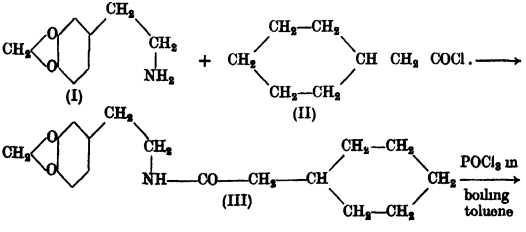

(A)

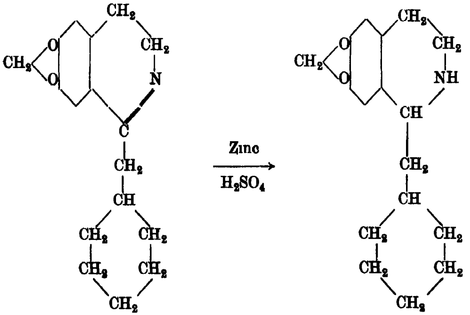

(B)


(C)

1-Cyclohexyl isoquinoline.

The scheme outlined below represents the various steps in the synthesis of 1-cyclohexyl isoquinoline ·





Cyclohexyl malonic acid was prepared by the reduction and hydrolysis of ethyl cyclohexylidene cyano-acetate obtained by the condensation of cyclohexanone and ethyl cyano-acetate (Harding, Haworth, and Perkin, *J Chem Soc*, 1909, *93*, 1943, Vogel, *J Chem Soc*, 1928, 2023)

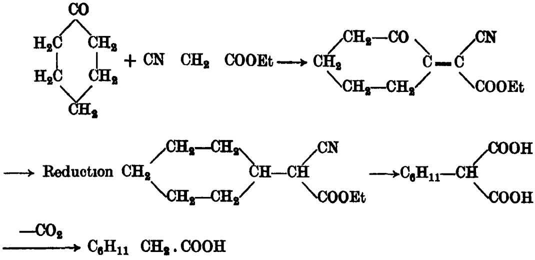
The malonic acid was heated under reduced pressure in an oil bath when decarboxylation took place and the cyclohexyl acetic acid distilled over This was converted by treatment with thionyl chloride into cyclohexyl-acetyl chloride which, in presence of aqueous alkali, reacted with homopiperonyl amine to give cyclohexyl-acetyl-β-3 4,methylenedioxy-phenyl ethyl amide (M P 128°)

The amide, in presence of phosphoryl chloride in boiling toluene, gave 1, cyclohexyl-methyl-6 . 7,methylenedioxy-3 . 4,dihydroisoquinoline M P 100° The hydrochloride in a dilute solution exhibits a strong blue fluorescence Reduction of the base with zinc spangles and sulphuric acid gave the tetrahydro base which could not be crystallized successfully, probably owing to its low melting point The tetrahydro base gave a sparingly soluble hydrochloride which showed only a very feeble fluorescence in a large volume of water The reduced base gave a sticky benzoyl derivative which could not be crystallized The *p*-nitro-benzoyl derivative, however, was prepared in a pure crystalline condition

Experiments are in progress with cyclohexane carboxylic and dekalin carboxylic acids

EXPERIMENTAL

Cyclohexyl acetic acid was prepared from cyclohexanone according to the scheme outlined below :—



Preparation of cyclohexylidene cyano-acetate

(Harding, Haworth and Perkin, *Journ Chem Soc*, 1908, *93*, 1943)

Equimolecular proportions of cyclohexanone (9 8 g) and ethyl cyano-acetate (11 3 g) were mixed with a few drops of piperidine and allowed to stand for a few minutes Condensation takes place readily with the separation of water

The product was heated on the water bath for two hours, diluted with water, and extracted with ether The ether extract was washed with dilute hydrochloric acid, dried over anhydrous calcium chloride and the solvent removed The pale yellow oil was distilled under reduced pressure (165°-67°/15 mm)

151°/12 mm $n_D^{18°} = 1\ 4974$ (Vogel, *Journ Chem Soc*, 1928, 2023)

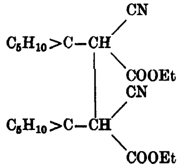
160°-63°/15 mm (Lapworth and MacRae, *Journ Chem Soc*, 1922, *121*, 2754)

151°/10 mm $n_D^{19\ 5°} = 1\ 49670$ (Birch, Kon and Norris, *Journ Chem Soc*, 1923, *123*, 1373)

Ethyl r-cyclohexyl cyano-acetate

(Vogel, *ibid*, 2023)

The unsaturated ester (10 0 g) was reduced with moist aluminium amalgam (15 0 g), there was a period of induction of about three hours and the reaction was complete after nine hours, when the product was worked up in the usual fashion and distilled Ethyl-*r*-cyclohexyl cyano-acetate (8 5 g.) passed over at 144–46/14 mm. The viscid residue was dissolved in methyl alcohol and the solvent evaporated in vacuum over concentrated sulphuric acid and traces of impurities removed by extracting with boiling light petroleum, when it melted at 87°. It was the bimolecular product,



The liquid reduction product, on redistillation, boiled at 145°/14 mm and had $n_D^{18\cdot5^\circ} = 1{\cdot}4612$

Cyclohexyl malonic acid

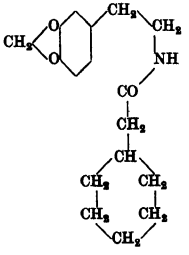
(Vogel, *Journ Chem Soc*, 1928, 2023)

A solution of ethyl cyclohexyl cyano-acetate (20 g) in rectified spirit (40 g) and a solution of potassium hydroxide (30 g) in water (60 c c) was refluxed for 18 hours and evaporated to dryness An aqueous solution of the residue was shaken with ether to remove unchanged substance, acidified and the precipitated acid filtered The acid mother liquor, on extraction with ether, yielded some more of the acid M P 178° The yield was nearly quantitative The acid was purified by dissolving in $NaHCO_3$ solution and precipitating with HCl

Cyclohexyl acetic acid

Cyclohexyl malonic acid (6 g) was distilled under reduced pressure from an oil-bath, when decarboxylation took place The acetic acid distilled at 117°/5 mm Yield, 2 g A considerable amount of a non-acidic material was left behind in the flask, which was not investigated (Cf Hope and Perkin, *Journ Chem Soc*, *95*, 1364, they report the preparation of the acid in good yields by keeping the malonic acid at 180°, but do not record the formation of the non-acidic substance)

Cyclohexyl-acetyl-β-3 4-methylenedioxy-phenyl ethylamide



Cyclohexyl acetic acid (2 65 g) was carefully mixed with thionyl chloride (1 86 c c) when a vigorous reaction set in with copious evolution of hydrogen chloride The reaction was completed by heating the mixture on the steam-bath for half an hour The syrupy liquid was added in small portions to an ice cold emulsion of homopiperonylamine (3 0 g), in a solution of 10 per cent potassium hydroxide (20 c c) with vigorous shaking after each addition After the addition was complete, the product was allowed to stand in an ice-bath for 10 minutes and filtered The residue was thoroughly washed with petroleum ether and dried in vacuum desiccator The dried amide crystallized from alcohol (charcoal) in fine, long needles melting at 128° Yield, 4 9 g

16 36 mg of the amide (dried in vacuum) gave 0 760 c c 'N_2' at 32° and 763 mm pressure

Found N, 5·23 per cent

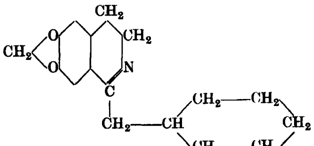
$C_{17}H_{23}O_3N$ requires N, 4 85 per cent

17 10 mg gave 44 44 mg of CO_2 and 12 73 mg of H_2O

Found C, 70 87, H, 8 27 per cent

$C_{17}H_{23}O_3N$ requires C, 70 55, H, 8 02 per cent

1-Cyclohexyl-6 7-methylenedioxy-3 4-dihydroisoquinoline



The above amide (2 0 g) was suspended in dry toluene (15 c c) and phosphorus oxychloride (10 c c) added The mixture became warm and was then refluxed for 2½ hours at 120°–130° The fluorescent toluene solution was cooled and petroleum ether added till there was no more separation of a crystalline precipitate. The precipitate was collected at the pump, washed well with petroleum ether and treated with 15 c c hot water containing 2 5 c c concentrated hydrochloric acid. The hot solution was filtered, cooled and ether extracted The acid layer was freed from ether by warming on a water-bath, cooled to 0°C , and basified with liquor ammonia. The base separated as an amorphous powder on standing When the base was crystallized slowly from dilute alcohol, it separated in long silky needles Yield, 1·5 g. M.P. 100°.

The base dissolves easily in alcohol and moderately in benzene and ether. When shaken with water, it exhibits a bright blue fluorescence.

18 37 mg (dried in vacuum) gave 0 87 c c of nitrogen at 31·5°C and 759 4 mm. pressure ; 22 98 mg gave 63 12 mg of CO_2 and 16·56 mg. of H_2O.

Found C, 74 91, H, 8 01, N, 5 30 per cent
$C_{17}H_{21}O_2N$ requires C, 75 23, H, 7 81, N, 5 16 per cent

The platinichloride

The base (0 5 g) was dissolved in 3 c c hydrochloric acid (1 1) and treated with a solution of 5 per cent chloroplatinic acid till there was no more precipitate formed The light yellow amorphous solid was collected at the pump, washed well with water, and then with a little dilute alcohol After drying in the steam oven it melted at 204° (decomp)

44 3 mg of the platinum salt (dried in vacuum at 100°) gave 9 287 mg of platinum

Found Pt, 20 96 per cent
$(C_{17}H_{21}O_2N)_2$ H_2PtCl_6 requires Pt, 20 49 per cent

The hydrochloride

The base (0 1 g) was rubbed with concentrated hydrochloric acid (1 c c) and kept overnight in vacuum The solid was crystallized from hot absolute alcohol which deposited glistening plates melting at 188°-189° The salt is very hygroscopic and becomes sticky on exposure to air for a few minutes Its solution in water exhibits a mild blue fluorescence

38 44 mg (dried in vacuum) required 5 4 c c of 1 108 N/50 NaOH

Found Cl, 11 04 per cent
$C_{17}H_{21}O_2N$ HCl requires Cl, 11 5 per cent

The picrate

The base (0 1 g) was dissolved in dilute hydrochloric acid (3 c c) and a concentrated solution of picric acid was added The picrate was collected at the pump and crystallized from acetone Short, stout needles melting at 162°

16 92 mg gave 1 64 c c of nitrogen at 763 mm pressure and 32°C

Found N, 11 15 per cent
$C_{17}H_{21}O_2N$ $C_6H_3O_7N_3$ requires N, 11 10 per cent

1,Cyclohexyl-6 7,methylenedioxy-1 2 3 4,tetrahydro-isoquinoline

The dihydro base (1 g), zinc spangles (3 g) and copper sulphate (0 05 g) were taken in water (35 c c) and concentrated sulphuric acid (3 c c) added in the course of an hour to the mixture heated on a water-bath Heating was continued for another hour after addition and the product filtered hot The residue was treated with boiling water thrice (10 c c each time) and filtered. The combined filtrate was cooled and basified with excess of ammonia The sticky precipitate was extracted with ether, the extract dried over anhydrous potassium carbonate and the solvent removed The residue that was left was also sticky and could not be crystallized successfully. It was therefore converted into the pure hydrochloride by dissolving in dilute hydrochloric acid, evaporating the solution to dryness on a water-bath and crystallizing from dilute alcohol It separated in plates, melting at 214°

The *hydrochloride* is sparingly soluble in cold but dissolves readily in hot water, the solution exhibiting a blue fluorescence

39 21 mg (dried at 100°) requires 5 7 c c of 1 108 N/50 NaOH

10 12 mg gave 0 514 c c of nitrogen at 759 9 mm and 33°C

Found Cl, 11 43, N, 4 50 per cent

$C_{17}H_{24}O_2NCl$ requires Cl, 11 47, N, 4 52 per cent

The *p-nitrobenzoyl derivative* was prepared by suspending the reduced base (0 1 g) in 10 per cent potassium hydroxide solution (5 c c), adding *p*-nitrobenzoyl chloride (0 5 g) in small quantities and shaking vigorously

The separating solid was collected, washed well with dilute alkali and then with water, dried, and the solid triturated successively with small amounts of petroleum ether and dry ether The residue crystallized from boiling alcohol in glistening plates, melting at 164°

20 84 mg (dried in vacuum) gave 1 245 c c of nitrogen at 759 7 mm and 32°C

Found N, 6 69 per cent

$C_{24}H_{26}O_5N_2$ requires N, 6 63 per cent

The *picrate*, prepared in the usual manner, crystallized from dilute alcohol in felted leaflets, melting at 178°

15 00 mg gave 1 443 c c of nitrogen at 761 3 mm and 31°C

Found . N, 11 08 per cent

$C_{17}H_{23}O_2N$ $C_6H_3O_7N_3$ requires N, 11 15 per cent.

PRESIDENCY COLLEGE,
MADRAS,
30th November, 1939

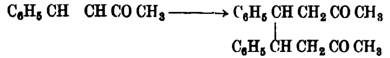
STUDIES IN THE ISOQUINOLINE SERIES

PART VIII 1,1′-BIS-TETRAHYDRO-ISOQUINOLINES

By B B DEY *and* T R GOVINDACHARI

(*Read January 2, 1940*)

As early as 1896, Harries and Eschenbach (*Ber* , 1896, *29*, 380), while reducing benzylidene acetone with moist sodium or aluminium amalgam, observed the formation of a dimolecular reduction product with a coupling at the β-position, thus



$$C_6H_5\,CH\quad CH\,CO\,CH_3 \longrightarrow \begin{array}{l} C_6H_5\,CH\,CH_2\,CO\,CH_3 \\ \quad\quad\ \ | \\ C_6H_5\,CH\,CH_2\,CO\,CH_3 \end{array}$$

Harries and co-workers (*Ann* , 1897, *29*, 380, *Ber* , 1898, *31*, 1806 , *Ann* , 1904, *330*, 235) extended the study of these reductions to benzylidene acetophenone, methyl cyclohexanone, phorone, mesityl oxide and other similar compounds, and in all these cases obtained evidence of the formation of dimolecular reduction products

Higginbotham and Lapworth (*J C S* , 1923, *129*, 594) have advanced the adsorption theory to account for the formation of these dimolecular products A part of the molecules are supposed to be first adsorbed, and these then attacked by the other molecules still in solution Two layers of simple molecules would then be formed one above the other, changing ultimately into one layer of double molecules by readjustment of electrons in the whole complex system made up of the molecules as well as the metal and the solvent Alternatively, the individual molecules of the interacting pairs, which lie side by side, form part of the layer of molecules directly attached to the metal, and by subsequent readjustments of electrons in the systems, unite in pairs

Israel Vogel has accepted the above theory as the most feasible, and as a result of a number of investigations on the reductions with aluminium amalgam of compounds of the type $CR_1R_2 = CR_3R_4$, where R_1, R_2 are groups or ring systems, and R_3, R_4 are H, CN, COOEt or COOMe (*J C S* , 1927, 129, 594, 1985, *ibid* , 1928, pp 1017, 2010, 2032), has arrived at certain general conclusions as follows —

1 The extent to which dimolecular reduction products are formed depends on the groups R_1, R_2 The larger the volumes of these groups, the less the chances of dimolecular products being formed
2. Other conditions being comparable, the nature of the compounds formed and their yields are controlled by the thickness and therefore the surface of the aluminium foil

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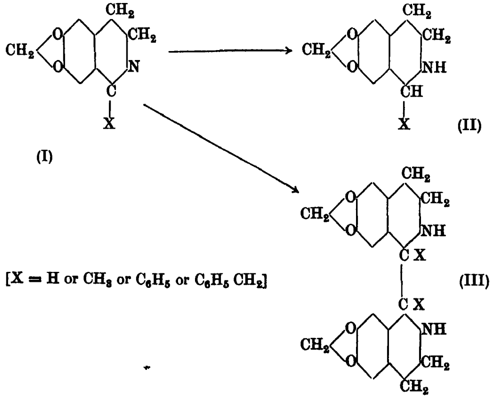
The reduction of substituted 3 4 dihydro-isoquinolines with aluminium amalgam, described in this communication, was undertaken with a view to study if such dimolecular products were formed at all during the reduction of the C = N linkage, and if so, how far the yields of these products were controlled by the nature and volume of the substitutent attached to C-atom in position 1

Norhydrastinine (6 7-methylene-dioxy-3 4-dihydro-isoquinoline) gave only about 15 per cent of the dimolecular products (1,1′-bis-norhydrohydrastinine) and about 55 per cent of the normal tetrahydro base, norhydrohydrastinine, while 1 methyl-norhydrastinine gave as much as 60–70 per cent of 1,1′ bis-methyl-norhydrohydrastinine and only 5–10 per cent of 1,methyl-norhydrohydrastinine On the other hand, with 1,phenyl-norhydrastinine, the normal reduction product, 1,phenyl-norhydrohydrastinine appeared to be exclusively formed (nearly 95 per cent), no evidence of the formation of any dimolecular reduction product being found Again, 1-benzyl norhydrastinine gave 60 per cent of the dimolecular compound (1-1′-bis-benzyl norhydrohydrastinine) and 30 per cent of the monomolecular product, 1-benzyl norhydrastinine The analytical data for the latter compounds are not yet complete, and this, together with the reduction of 1,cyclohexyl-, and 1,cyclohexyl methyl-norhydrastinine, will form the subject of a later communication

The reduction of the various isoquinolines studied in this paper is represented in the following scheme —



(I)

(II)

(III)

[X = H or CH_3 or C_6H_5 or $C_6H_5\,CH_2$]

Norhydrastinine, and the 1,methyl- and 1,phenyl-derivatives appear to have been synthesised by Decker and Becker (*Ann*, 1913, *395*, 313), but complete details have not been given by the authors They are now described in full

EXPERIMENTAL

The aluminium amalgam required in these reductions was prepared according to the method of Vogel (*J C S*, 1927, p 597) with the difference that a 0 5 per cent instead of a 2 per cent solution of mercuric chloride was used

Norhydrastinine

2 gms of homopiperonylamine were dissolved in 10 c c of dry ether and treated drop by drop with 0 6 gm of anhydrous formic acid The ether was then distilled off, and the salt heated in a small flask fitted with a cork carrying a $CaCl_2$-tube, to 180° 200° for 2 hours After cooling, 8 c c of dry toluene and then 4 c c of phosphoryl chloride were added and the solution was heated on an oil-bath to 120° for one and half hours On cooling, 15 c c of petroleum ether were added, allowed to stand for 15 minutes, and the toluene-petroleum ether layer decanted off The gummy residue was dissolved in water, extracted with ether to remove non-basic impurities, cooled in ice and basified with caustic soda The oil that separated was extracted with benzene, the benzene extract dried over solid potash and the benzene distilled off 1 65 gm of crude norhydrastinine (M P 83°-85°) were thus obtained Recrystallisation from ligroin gave 1 4 gm of the pure product M P 90°-91°

Reduction of norhydrastinine with aluminium amalgam

2 gms of norhydrastinine were added to 2 5 gms of aluminium amalgam in 75 c c of moist ether The flask was fitted with a double surface condenser and cooled in a large trough of cold water to minimise loss of ether The evolution of hydrogen was found to cease immediately after the addition of the isoquinoline but was resumed after what might be called an induction period of 15-20 minutes The reduction was allowed to proceed for 48 hours, a few drops of water being added at the end of 24 hours The ether was filtered off, the residue ground thoroughly with more ether, and again filtered (Residue A)

The combined ether extracts left on distillation, 1 4 gm of a mixture of solid and oil This was treated with 10 c c of rectified spirits, warmed slightly, cooled and then filtered 0 2 gm of a solid was obtained which, after slow crystallisation from acetone, melted at 226°-227° White prismatic blocks

The alcoholic filtrate gave, on evaporation, 1 15 gm of oil Treatment with rectified spirits was repeated if there was any sign of solid particles The oil gave a nitroso-derivative crystallising in flat square plates M P 226° This was proved to be identical with the nitroso-derivative of norhydrohydrastinine prepared by the reduction of norhydrastinine with zinc and sulphuric acid

Residue A was dissolved in 20 c c of 4N HCl, filtered, treated with alkali until the solution remained slightly acidic, and precipitated with picric acid The picrate (0 25 gm) melted at 220°- 221° after crystallisation from acetic acid (rhombic blocks) This was found to be identical with the picrate of the compound, M P 226°-227°, obtained from the ethereal solution and it could be converted into the free base in the usual way

1-1′, bis-norhydrohydrastinine, (III, X = H), M P 226°-227°

16 63 mg of substance dried in vacuum gave 1 2251 c c of nitrogen at 33° and 757 6 mm pressure

Found N, 8 19 per cent

$C_{20}H_{20}O_4N_2$ requires N, 7 90 per cent

The platinichloride, M P 299° (decomp)

0536 gm gave ·0091 gm of platinum

Found Pt, 16 97 per cent

$[C_{20}H_{20}O_4N_2]_2\ H_2PtCl_6$ requires Pt, 17 5 per cent

$C_{20}H_{20}O_4N_2\ H_2PtCl_6$ requires Pt, 25 75 per cent

The nitroso-derivative Thick rhombic needles from alcohol M P 218° (d)

11 42 mg gave 1 1792 c c of N_2 at 28° and 764 3 mm

Found N, 11 79 per cent

$C_{20}H_{18}O_6N_4\ 2H_2O$ requires N, 11 66 per cent

Benzoyl derivative Clusters of tiny rhombic needles from alcohol M P 263°

Picrate Crystallised from acetic acid as thick rhombic plates M P 220°-221° (decomp)

Methiodide, M P 225°—sparingly soluble in alcohol, unlike the methiodide of norhydrohydrastinine

1, methyl-6, 7-methylenedioxy-4, 5-dihydroisoquinoline

2 gms of homopiperonylamine were dissolved in 10 c c of dry ether, and treated with 1 5 gm of acetic anhydride drop by drop The ether was then distilled off, and the thick oil left behind was treated with 8 c c of dry toluene and 2 c c of $POCl_3$ and kept at 120°-130° for one and a half hours After cooling, 20 c c of petroleum ether were added, allowed to stand for 10 minutes and the toluene-petroleum ether was decanted off The gummy residue was dissolved in 30 c c of water, and extracted with ether to remove non-basic impurities The acid solution was then strongly cooled and basified with caustic soda The oil that separated was extracted with benzene dried over caustic potash and the benzene distilled off The oil that was left behind solidified immediately Yield, 2 1 gm M P. 81°-88° raised to 92° on crystallisation from ligroin.

Reduction of the above isoquinoline with aluminium amalgam

2 gms. of the isoquinoline were added to 2 5 gms. of aluminium amalgam in 75 c c of moist ether and the experiment conducted in the same way as with norhydrastinine Shiny white crystals began to separate soon after the initial period of induction, during which hydrogen ceased to be evolved, was over, but the reaction was allowed to proceed as usual for 48 hours

The solid residue in the flask was filtered from the ether, ground up thoroughly with more ether, and again filtered (Residue A) The collective ether filtrates left on distillation a mixture of solid and oil This was treated with about 10 c c of rectified spirits The oil dissolved, and the undissolved solid was filtered off This melted at 162° and after recrystallisation from acetone, melted at 165° Rhombic plates Yield, 0 1 gm It is practically insoluble in cold alcohol and dissolves sparingly in benzene, ether, ligroin, and more readily in hot acetone and chloroform

The alcoholic filtrate gave, on evaporation under reduced pressure in a desiccator, only 0 1 gm of an oil which readily formed a sparingly soluble hydrobromide, M P 268°, and a picrate, M P 185° identical with the hydrobromide and picrate respectively of 1,methyl 6,7-methylene dioxy-1,2,3,4-tetrahydroisoquinoline

Residue A was ground up in a mortar with 30 c c of 8N HCl, filtered, and the cooled filtrate nearly neutralised with caustic soda solution, and then precipitated with picric acid The picrate was collected, washed with water, ground up with 20 c c of 8N HCl, and the liberated picric acid removed by repeated extraction with ether The aqueous layer was then strongly cooled and basified with ammonia, the precipitated base was filtered, washed repeatedly with distilled water, and then with cold rectified spirit Yield, 1·2 gm M P 164°, after softening at 162° Recrystallisation from acetone gave rhombic plates, M P 165°, identical with the solid obtained from the ethereal filtrate

1-1′,bis-methyl-norhydrohydrastinine, (III, X = CH_3), M P 165°

15·98 mg of substance gave 40 94 mg of CO_2 and 9 29 mg of H_2O
22 38 mg of substance gave 1 523 c c of N_2 at 38° and 756 3 mm
$C_{22}H_{24}O_4N_2$ requires C, 69 47, H, 6 32, N, 7 37 per cent
Found C, 69 87, H, 6 48, N, 7·46 per cent
$C_{22}H_{24}O_4N_2$ requires C, 69 47, H, 6 32, N, 7 37 per cent

Picrate Laminated crystals, M P 164°

10·36 mg gave 1 215 c c of nitrogen at 32°C and 760 8 mm
Found N, 13 14 per cent
$C_{34}H_{30}O_{18}N_8$ (dipicrate) requires N, 13 37 per cent

The nitroso-derivative

0·2 gm of the bis-isoquinoline was dissolved in 5 c c of HCl, cooled in a freezing mixture, and treated with 5 drops of a saturated solution of $NaNO_2$

with stirring The white solid which separated was filtered quickly, washed thoroughly with cold distilled water, and dried in a vacuum desiccator over $CaCl_2$ It was crystallised from a small amount of hot acetone, avoiding prolonged boiling

M P 160°, with decomposition and evolution of gas

23 53 mg gave 2 6876 c c of nitrogen at 36° and 755 75 mm

Found N, 12 54 per cent

$C_{22}H_{22}O_6N_4$ (dinitroso-derivative) requires N, 12 76 per cent

The platinichloride, M P 240°

0961 gm of platinichloride gave 0158 gm of platinum

Found Platinum, 16 44 per cent

$(C_{22}H_{24}O_4N_2)_2$ H_2PtCl_6 requires Pt, 16 67 per cent

$(C_{22}H_{24}O_4N_2)$ H_2PtCl_6 requires Pt, 24 71 per cent

Although there are two basic nitrogen atoms in the bis-isoquinoline molecule, the analytical values for platinum indicate that two such bis-isoquinoline molecules have combined with one molecule of H_2PtCl_6, as if it was a mono-acid base

1,phenyl-norhydrastinine

2 gms of homopiperonylamine were benzoylated in the usual way and gave 3 0 gms of pure benzoyl homopiperonylamine after crystallisation from rectified spirits M P 119°-120°

3 0 gms of benzoyl homopiperonylamine were heated with 8 c c of $POCl_3$ on the boiling water-bath for one and a half hours and then poured on to crushed ice The solution was filtered, cooled, made alkaline with caustic soda and extracted with benzene The benzene extract was dried over solid caustic potash and the benzene distilled off The crude product weighed 2 6 gms and melted at 134°–136° Recrystallisation from ligroin gave 2 1 gms of the pure isoquinoline M P 138°

Reduction of 1-phenyl-norhydrastinine with aluminium amalgam

2 gms of the above compound were reduced with 2 5 gms of amalgam in 75 c c of moist ether in precisely the same way as before The usual induction period of 5 minutes was observed also in this case The ethereal solution was filtered, the residue ground up with more ether, and again filtered The combined ether filtrates gave 1 95 gm of a solid, M P 97°-98°, with only slight sintering at 95° On crystallising from ligroin, it melted at 98° The hydrochloride, prepared by rubbing the compound with aqueous HCl, melted at 280°-281° The substance was proved to be identical with 1-phenyl-norhydrohydrastinine in all respects Not a trace of the dimolecular product could be observed in this case

PRESIDENCY COLLEGE,
MADRAS,
12th December, 1939.

ON THE THEORY OF A SYSTEM OF RECEDING PARTICLES HAVING A TENDENCY TO APPROACH THE CENTRAL MASS

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(Communicated by Prof G S Mahajani, Ph D)

(*Read March 11, 1940*)

I INTRODUCTION AND FORMULATION OF THE NEW EQUATIONS OF MOTION

Milne has given a theory of a system of particles moving within a sphere of radius $r = ct$ at an epoch t such that the speed of any individual particle increases with the distance The space (3-dimensional) in which the particles are supposed to move is 'flat', and it is also supposed to be devoid of any irregularities as to its structure, it being assumed that the material contents are swept away to $r = ct$ The space within the sphere $r = ct$, therefore, is homogeneous but not, in general, isotropic, it will be shown below that it is isotropic only for $G(\xi) = -1$ Hence, such a smoothed out universe is called a 'substratum' This has been accepted to be a possible form of a world-model The theory associated with such a model has been termed the Kinematical Theory of Relativity, and it centres round the following path-equations for the system of particles having a motion of recession, viz

$$\frac{dV}{dt} = (P - Vt)\frac{Y}{X}G(\xi) \qquad . \qquad (1)$$

where

$$X = t^2 - P^2/c^2, \quad Y = 1 - V^2/c^2, \quad Z = t - \frac{P\ V}{c^2}, \quad \xi = \frac{Z^2}{XY}, \quad P = \surd(x^2+y^2+z^2),$$

$V = (u, v, w)$, $\frac{dx}{dt} = u$, etc , the notation being the same as that given by Milne These are the equations of motion for the kinematical system regarded as a statistical system with a distribution function $\frac{Bt dx dy dz}{c^3(t^2 - P^2/c^2)^2}$, the particles moving away from the observer (who is supposed to be situated at the centre of the nuclear cluster) with speed increasing with the distance Here, the explicit assumption is that the attraction of the nuclear cluster on this receding swarm of point masses is negligible in comparison to the force tending the outward motion This uniformly increasing outward motion in every direction gives an idea of the homogeneity of structure for the smoothed out universe, but the isotropy of pressure is not, in general, satisfied by this model as can be shown by having recourse to a general line-element for

Published July 30th, 1940.

Milne's case This line-element has been shown by Walker[1] to be of the form

$$ds^2 = \{F(X)\}^2\left[dt^2 - \frac{1}{c^2}(dr^2 + r^2 d\theta^2 + r^2 \sin^2\theta d\phi^2)\right] \tag{2}$$

where $X = t^2 - \frac{r^2}{c^2}$ The condition of isotropy, viz

$$B^r_{ihk} = b\left(a_{ik}\delta^r_h - a_{ih}\delta^r_k\right) \tag{3}$$

where b is the Riemannian curvature, and the δ's are the Kronecker deltas, and $a_{11} = -\frac{1}{c^2}$, etc , in this case reduce to equations of the form

$$B^j_{iji} = B^k_{iki}, \; j \neq k \tag{4}$$

which, in turn, leads to the following differential equation for $F(X)$, viz

$$F\frac{d^2F}{dX^2} - 2\left(\frac{dF}{dX}\right)^2 = 0 \tag{5}$$

The complete integral of (5) is

$$F = (aX + b)^{-1} \tag{6}$$

where a and b are arbitrary constants If in (6) we put $b = 0$ and $a = t_0^{-2}$, (2) then gives a line-element for the case $G(\xi) = -1$ This line-element has been termed by Gilbert[2] as the 'Metric of the Substratum'

Although, in reality, the condition of isotropy and homogeneity do not exactly hold good, this assumption is not very far from the true state As it is, it should be remembered that (1) does not actually represent the motion of a system of particles in a slightly inhomogeneous material distribution in a possible form of a world-model The slight irregularities here and there due to the non-homogeneity of the model under consideration are not supposed to destroy the property of an isotropic pressure to any appreciable extent for the particular case $G(\xi) = -1$ Thus, as a matter of fact, the receding particles are attracted by other masses (including the nuclear cluster) which are excluded from the 'domain' forming the statistical system This 'extraneous' influence would naturally tend to hinder the outward motion and the recession of particles cannot 'go on' indefinitely For the purpose of simplicity, let us assume that the space $r = ct$ is smoothed out of any inhomogeneous matter except the nuclear cluster so that the particles are attracted towards the central mass only Let R be the radius of the model under consideration at any epoch t, so that $R = ct$ The law of recession at such a great distance is

$$\dot{r} = V = \frac{r}{t} \quad . \quad . \tag{7}$$

Therefore, for $r \sim ct$ we have

$$X = \dot{\epsilon}\; t^2,\; Y = \epsilon,\; Z = \epsilon\; t,\; \xi = 1, \quad . \quad .. \tag{8}$$

where $\epsilon = 1 - \frac{P^2}{c^2 t^2}$. Hence, the acceleration formula reduces to

$$\frac{dV}{dt} \sim 0 \tag{9}$$

This would give zero acceleration for any particle of the system, so that a thick 'horizon' would be formed on the surface of the sphere $r = R$ So, it is natural to suppose that the motion of particles of the non-homogeneous system is reversed after they reach the limits of the model and the modified equations of motion for these particles incorporating this tendency to 'go back' can be expressed as a single vector relation

$$\frac{dV}{dt} = (P - Vt)\frac{Y}{X}G(\xi) \pm YZH(X, \xi) \tag{10}$$

which is invariant for Lorentz transformations In general, we have the vector relation, viz

$$\frac{dV}{dt} = (P - Vt)\frac{Y}{X}G(\xi) \pm Y^m Z^n H(X, \xi) \tag{11}$$

which is Lorentz-invariant provided $2m + n = 3$

It is possible to obtain equations (10) from the Principle of Least Action The procedure is similar to that used by Walker [8] We have the variational integral, viz

$$\delta \int W ds = 0 \quad .. \tag{12}$$

where $ds = Y^{\frac{1}{2}} dt$ Let $W(X, \xi) = X^{\frac{1}{2}} \xi^{\frac{1}{2}} U(X, \xi)$, then (12) can be written as

$$\delta \int (ZU) dt = 0 \quad . \quad . \quad . \tag{13}$$

which leads to the following variational equation

$$\frac{d}{dt}\left[\frac{\partial}{\partial V}(ZU)\right] - \frac{\partial}{\partial P}(ZU) = 0 \quad . \tag{14}$$

Let us put

$$A = \frac{Z}{Y}\xi\frac{\partial U}{\partial \xi}, \quad B = \frac{Y}{Z}A + \tfrac{1}{2}U,$$

also, we have

$$\frac{dX}{dt} = 2Z, \quad \frac{dY}{dt} = -2\left\{(tY - Z)\frac{Y}{X}G(\xi) \pm \frac{V}{c^2}YZH(X, \xi)\right\},$$

$$\frac{dZ}{dt} = Y - \left\{(tZ - X)\frac{Y}{X}G(\xi) \pm \frac{P}{c^2}YZH(X, \xi)\right\},$$

$$\frac{d\xi}{dt} = \frac{2Z}{X}(1 - \xi)(1 + G) \mp 2Y\xi\left(P - V\frac{Z}{Y}\right)\frac{H(X, \xi)}{c^2}$$

With the help of these relations, after considerable reduction, (14) reduces to

$$\left(V-\frac{Y}{Z}P\right)\left(\frac{dA}{dt}-tA\frac{Y}{X}G\right)\pm AtYH=0, \tag{15}$$

that is,

$$(P-Vt)\frac{dA}{dt}-tA\frac{dV}{dt}=0, \tag{16}$$

or,

$$\frac{d}{dt}\left[\log\left\{A(P-Vt)\right\}\right]=0. \tag{17}$$

(17) gives

$$\xi\frac{\partial U}{\partial \xi}=\frac{\alpha}{Z\left(P-V\frac{Z}{Y}\right)}, \quad . \tag{18}$$

where α is a constant of integration

The relation (14) can be written in terms of A as

$$A\frac{dU}{dt}=P\left[\frac{Y}{Z}\frac{dA}{dt}+\frac{A}{2Z}\frac{dY}{dt}\right]-V\frac{dA}{dt}, \tag{19}$$

or,

$$\frac{dV}{dt}=PL_1-VL_2, \tag{20}$$

where

$$L_1=\frac{Y}{AZ}\frac{dA}{dt}+\frac{1}{2Z}\frac{dY}{dt}, \quad L_2=\frac{1}{A}\frac{dA}{dt}=\frac{t\frac{dV}{dt}}{P-Vt}$$

Therefore,

$$L_1=\frac{Y}{Z}L_2-\frac{Y}{XZ}(tY-Z)G\mp\frac{V}{c^2}YH \quad . \tag{21}$$

Hence,

$$\frac{dV}{dt}=\left(P\frac{Y}{Z}-V\right)L_2-\frac{PY}{ZX}(tY-Z)G\mp\frac{PV}{c^2}YH, \tag{22}$$

that is,

$$\left(1-\frac{t}{Z}\right)\frac{dV}{dt}=-\frac{PV}{c^2}\frac{Y}{ZX}(P-Vt)\mp\frac{PV}{c^2}YH \quad . \tag{23}$$

which gives

$$\frac{dV}{dt}=(P-Vt)\frac{Y}{X}G\pm YZH$$

2 MECHANICAL PROPERTIES OF THE NEW EQUATIONS OF MOTION.

It has been shown before that at a great distance the relations (8) hold good and that the acceleration of an individual particle tends to zero For similar considerations the new equations of motion would give the following value for the acceleration at great distances

$$\frac{dV}{dt} = \pm \frac{KG(1)}{t^3} \tag{24}$$

Here we have put $H(X, \xi) = KX^{-2}G(\xi)$ where K is a constant It is not difficult to prove that $G(1) = -1$ (24) then comes out as

$$\frac{dV}{dt} = -\frac{K}{t^3} \tag{25}$$

It is, therefore, quite evident that for a system of particles to have a tendency to approach the central mass we must take the upper sign only for the second term on the r h s of equation (10) There is, therefore, no loss of generality if in place of (10) we take the equation of motion as

$$\frac{dV}{dt} = (P-Vt)\frac{Y}{X}\,G(\xi) + \frac{KYZ}{X^2}\,G(\xi) \tag{26}$$

If the radius of curvature of the trajectories given by (1) is ρ_0 and ρ is the radius of curvature of those given by (10), then

$$\frac{1}{\rho} = \frac{1}{\rho_0} + n, \quad . \tag{27}$$

where

$$\frac{1}{\rho_0} = \frac{c^2 YG(\xi)}{XV^3}\left[\frac{1}{c^2}(P-Vt)^2 - XY(\xi-1)\right]^{\frac{1}{2}} \tag{28}$$

and $n = n(P, V, t)$ which is positive Hence

$$\frac{1}{\rho} > \frac{1}{\rho_0},$$

or,

$$\rho_0 > \rho \quad . \quad . \quad .. \quad .. \tag{29}$$

which clearly indicates attraction towards the nuclear cluster

From (26) we can write down the acceleration formula as [4]

$$\frac{1}{Y^{\frac{1}{2}}}\frac{d}{dt}\left(\frac{V}{Y^{\frac{1}{2}}}\right) = \left\{\left(P - V\frac{Z}{Y}\right) + \frac{K\xi}{Z}\right\}\frac{G(\xi)}{X} \quad . \tag{30}$$

The equation (30) contains on its r h s a sum of two 'complementary' accelerations g_1' and g_2', and hence it can be expressed as

$$\frac{1}{Y^{\frac{1}{2}}}\frac{d}{dt}\left(\frac{V}{Y^{\frac{1}{2}}}\right) = g_1' + g_2', \quad . \tag{31}$$

where

$$g_1' = -\left(P - V\frac{Z}{Y}\right)\frac{1}{X} - \frac{K\xi}{ZX} = g_1 - \frac{K\xi}{ZX} \quad . \tag{32}$$

and

$$g_2' = -\frac{C\left\{\left(P - V\frac{Z}{Y}\right)\frac{1}{X} + \frac{K\xi}{ZX}\right\}}{(\xi-1)^{\frac{3}{2}}\psi(\xi)} = g_2 - \frac{C\frac{K\xi}{ZX}}{(\xi-1)^{\frac{3}{2}}\psi(\xi)} \tag{33}$$

Near a condensation (not necessarily the central mass), $\xi \to 1$, $X \to t^2$, $y \to 1$, etc, and we get

$$g_2' = -\frac{P-Vt}{|P-Vt|^3}\frac{Cc^3t}{\psi(1)} - \frac{KCc^3}{|P-Yt|^3\psi(1)} \tag{34}$$

The second term on the r h s of (34) gives the departure from the inverse square law for the system of particles considered here g_1 and g_2 are the values given by Milne

If g_2' be the component of local acceleration due to gravitation we get the force equation corresponding to (34) in the form

$$F' = F + \frac{MK\xi}{XZ}G(\xi) \tag{35}$$

where F is the force of gravitation for Milne's case (obeying the inverse square law), and it is given by

$$F = Mg_2 + \frac{V}{Y^{\frac{1}{2}}}\frac{1}{Y^{\frac{1}{2}}}\frac{dM}{dt}, \quad M = m\xi^{\frac{1}{2}} \tag{36}$$

If p' be the momentum when nuclear forces are present, and p be the momentum for Milne's case, then, we have

$$\frac{1}{Y^{\frac{1}{2}}}\frac{dp'}{dt} = M(g_1' + g_2') + \frac{V}{Y^{\frac{1}{2}}}\frac{1}{Y^{\frac{1}{2}}}\frac{dM}{dt}, \tag{37}$$

and

$$\frac{1}{Y^{\frac{1}{2}}}\frac{dp}{dt} = M(g_1 + g_2) + \frac{V}{Y^{\frac{1}{2}}}\frac{1}{Y^{\frac{1}{2}}}\frac{dM}{dt} \tag{38}$$

From (37) and (38) we deduce the relation

$$\frac{1}{Y^{\frac{1}{2}}}\frac{d(\delta p)}{dt} = \frac{MK\xi}{ZX}G(\xi), \tag{39}$$

where we put $p' - p = \delta p$

3. FORCE AND ENERGY EQUATIONS FOR THE NEW SYSTEM OF PARTICLES.

The origin O being situated at the centre of the nuclear cluster, the acceleration of the receding particles can be written as

$$\frac{dV}{dt} = -\left\{(P-Vt)\frac{Y}{X} + \frac{KYZ}{X^2}\right\} - \frac{C\left\{(P-Vt)\frac{Y}{X} + \frac{KYZ}{X^2}\right\}}{(\xi-1)^{\frac{3}{2}}\psi(\xi)} \tag{40}$$

If a condensation is determined by $[\psi(\xi)]_{\xi=1}$ = maximum, and, if

$$\psi(\xi)=\psi(1)e^{-\frac{(\xi-1)^2}{a^2}}\quad(a\to 0 \text{ as } \xi\to 1)$$

gives the inverse square law for the attraction, then as the departure from the inverse square law is not considerable in the present case, (40) can be written as

$$\frac{dV}{dt}=-\left\{(P-Vt)\frac{Y}{X}+\frac{KYZ}{X^2}\right\}-\frac{M\left\{(P-Vt)\frac{Y}{X}+\frac{KYZ}{X^2}\right\}}{M_0(\xi-1)^{\frac{3}{2}}}\tag{41}$$

where M is the mass of the condensation Let m_1 be the mass of the particle (P, V, t) Then the relation giving the interaction between m_1 and M under the influence of the nuclear forces is given by

$$\frac{1}{Y^{\frac{1}{2}}}\frac{d}{dt}\left[\frac{M_1V}{Y^{\frac{1}{2}}}\right]=-\frac{M_1\left\{\left(P-V\frac{Z}{Y}\right)+\frac{KZ}{XY}\right\}}{X}$$

$$-\frac{MM_1\left\{\left(P-V\frac{Z}{Y}\right)+\frac{KZ}{XY}\right\}}{M_0X(\xi-1)^{\frac{3}{2}}}+\frac{V}{Y^{\frac{1}{2}}}\frac{1}{Y^{\frac{1}{2}}}\frac{dM_1}{dt},\quad M_1=m_1\xi^{\frac{1}{2}},\tag{42}$$

where the force of attraction on m_1 due to M is

$$F_P=-\frac{MM_1\left\{\left(P-V\frac{Z}{Y}\right)+\frac{KZ}{XY}\right\}}{M_0X(\xi-1)^{\frac{3}{2}}}+\frac{V}{Y^{\frac{1}{2}}}\frac{1}{Y^{\frac{1}{2}}}\frac{dM_1}{dt}\quad.\tag{43}$$

and the time-component corresponding to F_P [i e , the time-component of the four-vector (F_P, F_t)] is

$$F_t=-\frac{MM_1\left\{\left(ct-c\frac{Z}{Y}\right)+\frac{KZ}{XY}\right\}}{M_0X(\xi-1)^{\frac{3}{2}}}+\frac{c}{Y^{\frac{1}{2}}}\frac{1}{Y^{\frac{1}{2}}}\frac{dM_1}{dt}\tag{44}$$

The energy equation can now be expressed as

$$F_P\left(\frac{V}{Y^{\frac{1}{2}}}-P\frac{Y^{\frac{1}{2}}}{Z}-\frac{K}{XY^{\frac{1}{2}}}\right)-F_t\left(\frac{c}{Y^{\frac{1}{2}}}-ct\frac{Y^{\frac{1}{2}}}{Z}-\frac{K}{XY^{\frac{1}{2}}}\right)=\frac{1}{Y^{\frac{1}{2}}}\frac{d}{dt}(c^2M_1)\tag{45}$$

which with the help of (43) and (44) yields the relation, viz ,

$$\frac{c^2XY-K(c-V)}{XY^2}\frac{dM_1}{dt}=\frac{c^2MM_1}{M_0Z(\xi-1)^{\frac{3}{2}}}+\frac{2K(\mu_P-\mu_t)MM_1}{M_0X^2Y(\xi-1)^{\frac{3}{2}}},\tag{46}$$

$$\mu_P=P-V\frac{Z}{Y},\ \mu_t=ct-c\frac{Z}{Y}.$$

The gravitational potential is given by the equation

$$\frac{d}{dt}(c^2M_1+\chi) = -\frac{KZ(c-V)m_1M}{M_0X^2Y(\xi-1)^{\frac{3}{2}}} \quad . \tag{47}$$

If $\chi = \chi(P, t)$, then the gravitational potential is determined by

$$\frac{\partial\chi}{\partial P} = \frac{m_1M\left\{\left(P-V\frac{Z}{Y}\right)+\frac{KZ}{XY}\right\}}{M_0X(\xi-1)^{\frac{3}{2}}}+\frac{V}{Y^{\frac{1}{2}}}\frac{1}{Y^{\frac{1}{2}}}\frac{dM_1}{dt} \tag{48}$$

and

$$\frac{1}{c}\frac{\partial\chi}{\partial t} = -\frac{m_1M\left\{\left(ct-c\frac{Z}{Y}\right)+\frac{KZ}{XY}\right\}}{M_0X(\xi-1)^{\frac{3}{2}}}-\frac{c}{Y^{\frac{1}{2}}}\frac{1}{Y^{\frac{1}{2}}}\frac{dM}{dt} \tag{49}$$

Considering the condensation m as a simple point-mass just as m_1, the equation corresponding to (47) would be

$$\frac{d}{dt}[\chi+Mc^2] = -\frac{KZ(c-V)mM_1}{M_0X^2Y(\xi-1)^{\frac{3}{2}}} \tag{50}$$

If we put χ = the potential energy P E , $M_1c^2 = E_1$, $Mc^2 = E$, etc , then (47) and (50) give together the energy equation for the pair of two interacting particles m_1 and m as

$$\frac{d}{dt}[2\chi+E+E_1] = -\frac{KZ(c-V)(mE_1+m_1E)}{c^2M_0X^2Y(\xi-1)^{\frac{3}{2}}} . \tag{51}^*$$

Let us suppose that m is the mass of the nuclear cluster, m_1, m_2, , m_n are the masses of the receding particles, if the interaction of the particles amongst themselves be neglected, then the energy equation for this system of particles surrounding the nucleus of mass m is given by the relation, viz ,

$$\frac{d}{dt}\left[2n\chi+nE+\sum_{r=1}^{n}E_r\right] = -\frac{KZ(c-V)\left\{m\sum_{r=1}^{n}E_r+E\sum_{r=1}^{n}m_r\right\}}{c^2M_0X^2Y(\xi-1)^{\frac{3}{2}}} \tag{52}$$

If, however, the interaction between the particles themselves is comparable with that between the particles and the central mass, then the energy equation for the system can be written as:

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* It can be verified that

$$\frac{KZ(c-V)(mE_1+m_1E)}{c^2M_0X^2Y(\xi-1)^{\frac{3}{2}}}>0$$

Similar results can be obtained for the equations (52) and (53).

$$\frac{d}{dt}\left[(n+1)\chi+E+\sum_{r=1}^{n}E_r\right]=$$

$$-\frac{(n^2-n+2)}{2n}\cdot\frac{KZ(c-V)\left\{m\sum_{r=1}^{n}E_r+E\sum_{r=1}^{n}m_r\right\}}{c^2M_0X^2Y(\xi-1)^{\frac{1}{2}}}. \qquad . \quad (53)$$

It will be seen that the total energy for a pair of two interacting particles as given by (51) is negative Similarly, (52) and (53) give negative energy for the particular cases considered This negative value for the total energy of the three particular cases considered is, perhaps, due to a tendency of approach towards the nuclear cluster, present in the slightly non-homogeneous system of particles in (an approximately statistical) receding motion

4 SOME CONSEQUENCES RESULTING FROM THE NEW EQUATIONS OF MOTION

As an example of the tendency to approach towards the central mass exhibited by the system of particles considered here, let us take the system of particles given by $G(\xi)+1\sim 0$, $X\sim t^2$, $Y\sim 1$, $Z\sim t$, so that (26) is simplified to the form, viz ,

$$\frac{dV}{dt}\sim-\frac{P-Vt}{t^2}-\frac{K}{t^3} \qquad .. \quad .. \quad . \quad (54)$$

This system of particles is constrained to move under the influence of the central mass and the velocity of the constrained particle is now $\left(V-\frac{P}{t}-\frac{K}{2t^2}\right)$ instead of $\left(V-\frac{P}{t}\right)$ It is interesting to study the electrical state of this system of particles If m is the mass of each particle and e its charge, then the equation of motion of a particle of the system takes the form:

$$m\frac{dU}{dt}=eF-\mu U, \quad .. \quad .. \quad .. \quad .. \quad (55)[5]$$

where $F=(X, Y, Z)$ is the electric force, U the velocity of the constrained particle and μ is a constant In the present case, $U=V-\frac{P}{t}-\frac{K}{2t^2}$ (55) now reduces to

$$m\frac{d}{dt}\left(V-\frac{P}{t}-\frac{K}{2t^2}\right)=eF-\mu\left(V-\frac{P}{t}-\frac{K}{2t^2}\right). \qquad .. \quad (56)$$

Therefore,

$$\rho=\operatorname{div}F=\frac{m+\mu t}{et}\operatorname{div}V_1,\quad V_1=V-\frac{P}{t}, \quad .. \quad .. \quad (57)$$

where ρ is the density of the electric charge When ρ is not a function of position the equation of continuity [6] gives

$$\frac{d\rho}{dt}+\rho \operatorname{div} V_1 = 0 \qquad .. \quad (58)$$

From (57) and (58) we get

$$\frac{d\rho}{dt}+\frac{et}{m+\mu t}\rho^2 = 0 \qquad . \quad . \quad .. \quad (59)$$

which intergrates into

$$\rho^{-1} - \rho_0^{-1} = \frac{e(\mu t+m \log m)}{\mu^2} - \frac{em}{\mu^2}\log (m+\mu t), \qquad . \quad (60)$$

where ρ_0 is the initial density of charge The magnetic force $B = (\alpha, \beta, \gamma)$ is given by

$$curl B = \rho V_2 - \frac{mV_1}{et^2}+\frac{2Km}{et^4}, \quad V_2 = V - \frac{P}{t} - \frac{K}{2t^2}, \qquad . \quad (61)$$

the other equation remaining the same as in an earlier paper by the author The mechanical stress can be expressed as

$$(P, Q, R) = \rho\left\{\frac{(m+\mu t)V_2}{et} - \frac{mK}{2et^3}+[B \quad V_2]\right\} \qquad (62)$$

The rate at which work is done by the mechanical forces and the flow of energy per unit area (Poynting flux) are respectively given by

$$\frac{dW}{dt} = \rho V_2\left\{\frac{m+\mu t}{et}V_2 - \frac{mK}{2et^3}\right\} \qquad (63)$$

and

$$\pi = \frac{m+\mu t}{et}[B \quad V_2] - \frac{mKB}{2et^3} \qquad (64)$$

The points of difference between the system of particles considered here and the fundamental system (i e , the simple system) considered in a former paper can be clearly brought out from the above relations Two points of interest are: (1) the density of electric charge does not tend to zero as $t \to \infty$, and (2) the rate of change of the magnetic vector per unit time is the same for these two systems, although its magnitude is different for the two systems

It is a great pleasure to record my grateful thanks to Dr G S Mahajani for his keen interest in my work

5 SUMMARY

In this paper we have extended Milne's Kinematical Theory to a system of receding particles in a slightly inhomogeneous space with a dense cluster at the centre of the sphere $r = ct$ This system has, therefore, a tendency to approach the central mass due to the mutual attraction Equations of motion

are obtained for this new system of particles from the principle of least action These equations are given by (26) The attraction towards the nuclear cluster is also evident from the relation $\rho_0 > \rho$, where ρ is the radius of curvature of the space for the new system and ρ_0 is that for Milne's case Consideration of the energy equation for this system leads to a negative value for the energy-function from which it can be surmised that this must be due to the 'tendency of approach' towards the central cluster As an example, a system of charged particles conforming to the extended theory is considered and it is compared to the simple system of charged particles referred to above

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September 1, 1939.
Revised April 20th, 1940

STUDIES ON THE CHEMISTRY AND BIOLOGY OF THE SLOW SAND FILTERS AT THE MADRAS WATER WORKS

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(Communicated by Dr Gilbert J Fowler, D Sc , F I C)

(*Read January 2, 1940*)

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INTRODUCTION

The first sand filter generally referred to as the slow sand filter was built in 1829 by James Simpson for the Chelsea Water Company of London It was successful in removing turbidity and in improving the water hygienically The principle underlying its action was not understood until some years later Very soon however the use of sand filters was made compulsory for all river water supplies of Great Britain

The Metropolitan Water Board, London, now operate 178 slow and secondary sand filters, the total area of which is 175 64 acres The latest slow sand filters were constructed at Walton in 1926 Some of these filters have been working for almost a century and 'are still performing yeoman service' (Harold, 1935). In Europe sand filters are quite common and in Germany their use appears to be compulsory

Generally, slow sand filtration is to be preferred to other systems of purification as it purifies water in one simple process, removes tastes and odours due to algae to a marked degree, and ensures the supply of a safe water. Govinda Raju (1925-26) seems to prefer this system for India as in

[Published August 5th, 1940.

his view it does not involve the continuous addition of chemicals, as the waters of this country are practically free from suspended matter and as the cost of land is very cheap

But time has shown that slow sand filters in India have not been the unqualified success that they have been in England and on the continent The weight of opinion is still in favour of slow sand filters (Harold, *l c*) If in this paper statements are made against their use in India and in the tropics, it is not our intention to assail its universality It is only to investigate and prove that some changes in the method of purification are called for in view of the varying and variable conditions of the tropics

In several places in North and South India where slow sand filters are in use, the presence of H_2S has caused considerable anxiety to the water works authorities The use of slow sand filters in the following towns have really been disappointing At Agra (Stewart, 1933) in North India, at Baroda in West India, and at Adoni, Salem, Madras, Berhampur, Cocanada, Vizagapatam in South India (G W F C Reports) the filtrates from slow sand filters contain H_2S in considerable quantities

It may also be stated that slow sand filtration is not always an unfailing method of water purification from all points of view In one case the prevalence of goitre was attributed to inadequate purification by slow sand filters Robert McCarrison (1913-1914) in his 'Enquiry into the causation of goitre at the Lawrence Military Asylum, Sanawar' has stated that 'Another point of considerable interest is, that up to the year 1904 sand filters appear to have been employed with a view to the purification of the water So ineffectual were these, however, that their use was abandoned at the suggestion of the Chemical Examiner to the Punjab Government, who found that the water passed through them was considerably more impure than the untreated water' Further, 'the provision of a chemically and bacteriologically pure water is urgent, since apart from goitre, grave epidemics of water-borne diseases may at any time attack the people'

The present system of slow sand filtration at Madras has not been able to produce a potable water (*vide* various Reports of the Government Committee on Water and Sewage Purification and the periodical Reports of the Director, King Institute, Guindy, 1934) Two drawbacks noticed in the Madras slow sand filters are· (i) the production of H_2S in fairly large quantities, and (ii) the inability to supply at all times a water of uniform purity Regarding the first Dey and Ganapati (1934) have examined in detail the cause of the production of H_2S and have also isolated the causative organism responsible for it It is now proposed to examine the various physical, chemical and biological processes which take place in the Madras slow sand filters with a view to obtain an insight into the causes of their failure as an efficient purification process So this thesis is devoted to a study of the physical, chemical and biological conditions of· (1) the sources of the Madras Water Supply, (2) the raw water conduit (7·5 miles long) from the Red Hills Lake to the water

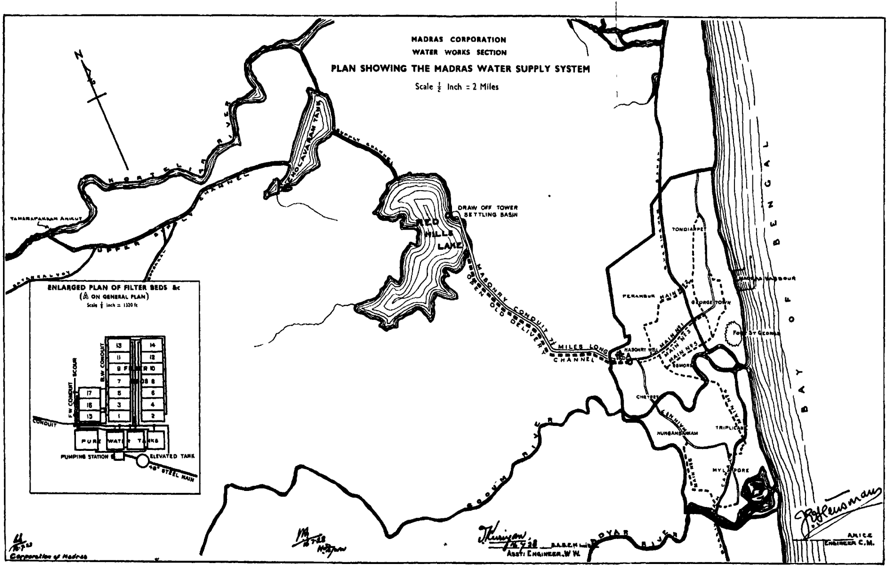

MADRAS CORPORATION
WATER WORKS SECTION
PLAN SHOWING THE MADRAS WATER SUPPLY SYSTEM
Scale ½ Inch = 2 Miles
N
KORTELLIAR RIVER
CHOLAVARAM TANK
SUPPLY CHANNEL
UPPER SUPPLY CHANNEL
TAMARAPAKKAM ANICUT
RED HILLS LAKE
DRAW OFF TOWER
SETTLING BASIN
MASONRY CONDUIT 7½ MILES LONG
OPEN OLD DELIVERY CHANNEL
MASONRY WELL
MAIN No 1
MAIN No 3
MAIN No 5
MAIN No 2
MAIN No 4
MAIN No 6
TONDIARPET
PERAMBUR
GEORGE TOWN
FORT ST GEORGE
MADRAS HARBOUR
EGMORE
CHETPET
NUNGAMBAKKAM
TRIPLICANE
MYLAPORE
COOUM RIVER
ADYAR RIVER
BAY OF BENGAL
ENLARGED PLAN OF FILTER BEDS &c
(A ON GENERAL PLAN)
Scale ⅛ Inch = 1320 ft
CONDUIT
F.W CONDUIT
SCOUR
B.W CONDUIT
FILTER BEDS
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
PURE WATER TANKS
PUMPING STATION
ELEVATED TANK
48" STEEL MAIN
Corporation of Madras
Asst. Engineer, W.W.
A.M.I.C.E
Engineer C.M.

Fig. 1.

works at Kilpauk where the slow sand filters are located, (3) the raw water prior to slow sand filtration, (4) the slow sand filters and their effluent, and (5) general summary and conclusion

CHAPTER I

1 *The Chemistry and Biology of the Sources of the Madras Water Supply*

'Some lake and reservoir waters may be applied to sand filters in their raw state ' Usually plain sedimentation is allowed to take place for twelve hours to three days to allow the suspended particles to go down to the bottom, the top water being taken to the filters

In the case of Madras, the sources of water supply are the Kortalayar river, Sholavaram Lake and Red Hills Lake (Fig 1) The water from the river is diverted by means of a low wall put across its breadth at a place called Tamarapakkam about 17 miles north-west of Madras The weir diverts the river excluding the greater flood discharges from the main river into a channel which leads to an artificial lake or reservoir called the Sholavaram Lake, wherein the water is stored and slowly sent lower down again by another channel into the Red Hills Lake So the water supply to the city is stored in two reservoirs, which also act as efficient settling tanks, as they hold many days' supply They insure an adequate supply of water even in times of drought for about a year Certain improvements in the physical, chemical and bacteriological qualities of a water are known to occur as a result of storage (Houston, 1914) These improvements seem to take place in tropical waters also (Cunningham and Raghavachari, 1920) But in the tropics the disadvantages accruing from the long storage of water seem to outweigh the beneficial effects of storage on account of algal growths (Fowler, 1923, King, 1931)

The real trouble in the case of Madras also seems to be due to algae It is now proposed to make a brief survey of the important physical, chemical and biological conditions of the two lakes, as such a survey will throw useful light on the various biochemical changes taking place in the slow sand filters at Kilpauk, which will be discussed in Chapter IV

The Sholavaram Lake

It is 2 miles long, 1 25 miles broad, and has a maximum depth of 16 feet At full tank level it has an area of 2 sq miles and a capacity of 583·3 m c ft It is a periodic lake which runs almost dry usually towards the end of the south-west monsoon season

The colour of the water varies from whitish-blue to yellowish brown It is whitish blue during the cold weather and north-east monsoon season, bluish green during the hot weather period and yellowish brown during the south-west monsoon season The temperature of the water is also high and is nearly uniform from surface to bottom The water is saturated with oxygen during the major part of the year Supersaturation also takes place sometimes during all seasons of the year Nutrient substances like phosphates, nitrites and nitrates are conspicuous by their absence Free ammonia is found only in traces, while albuminoid ammonia and oxidisable organic matter are found in considerable quantities

The macrophytic vegetation is found in abundance The aquatic vegetation consists chiefly of *Hydrilla verticellata*, *Vallisneria spiralis* and *Potomogeton natans*, which are found to cover the entire bottom of the lake during the south-west monsoon season (June to September) The phytoplankton is quantitatively poorly developed It is poor in Diatoms and Desmids, while Myxophyceae is dominant The dominant forms of Myxophyceae are *Microcystis aeroginosa*, *Microcystis marginata*, *Microcystis protocystis* and *Aphanothece* sp nov The zoo-plankton is also poorly represented and consists of 6 forms of Cladocera, one of Copepoda, one of Ostracoda, and nine forms of Nematoda

The bacterial quality of the water is found to vary from season to season Generally the water is of highest bacterial purity from the sanitary viewpoint during the hot weather and south-west monsoon season and of lowest purity during the north-east monsoon season

This lake may therefore be briefly characterised as a highly evolved, periodic, eutrophic lake

The Red Hills Lake

The Red Hills Lake which is also of the 'constant settlement' type has a catchment area of over 23 sq miles and receives water from Sholavaram Lake, which in turn is supplied by the Kortalayar river So the lake thus receives water that has travelled over an extensive area and has gathered considerable polluting and nutrient material Its catchment area is composed of grazing, agricultural and waste lands The soil around and at the bottom is composed of brown and red ochre earth laterite, which consists essentially of iron, silica and alumina and very little of lime and magnesia (Warth and Warth, 1903) Holland (1903) thinks that the relatives of the remarkable genera *Crenothrix*, *Cladothrix*, etc , which are active agents in the oxidation of ferrous salts, are sure to occur in newly-forming laterites. This statement is interesting in view of the occurrence of iron bacteria in the lake water and in the filtered water chambers of the slow sand filters at Kilpauk

The lake is 3 5 miles long with a maximum breadth of 2·5 miles and mean breadth of 2 0 miles and covers an area of 7 sq miles at its maximum level Its maximum depth is about 25 feet, and its capacity has been estimated at 2,162 m c ft

The water is yellowish green in colour and has a low transparency Its shores and bottom are not rocky but are heavily silted No permanent thermal stratification is seen in it but its temperature is high and is almost uniform from the surface to the bottom with circulation taking place continuously throughout the year The water is soft and alkaline but is extremely poor in nutrient salts like phosphates and nitrates. It is fairly well saturated with oxygen which is nearly homogeneously distributed from the surface to the bottom The content of free ammonia is extremely low but the amount of albuminoid ammonia and of oxidisable organic matter are great and are found in maximum during the end of the south-west monsoon season

It does not possess a broad zone of littoral vegetation and any distinct zonation of plants towards depth Its aquatic vegetation consists chiefly of *Potomogeton natans* and *Naias flexilis* Its phytoplankton is not quantitatively well developed and consists largely of blue-green algae *Aphanocapsa elachista* var *novo* and *Oscillatoria limnetica* Desmids and Diatoms are poorly represented

Bacteriologically the lake water is of fairly good quality Lactose fermentors are present in volumes of water varying from 60 c c to 1 c c and upwards and the total colonies per c c growing on nutrient agar at 37°C after 48 hours' incubation varied between 300 and 1,800

Besides these, the lake water is found to contain other physiological groups of bacteria such as iron bacteria, H_2S producing bacteria, colourless sulphur bacteria, purple coloured, sulphurless and sulphur containing bacteria and green coloured sulphur bacteria All these groups of bacteria do not occur as such but have been cultured from the Red Hills Lake water The existence of iron bacteria can be shown by carrying out a series of experiments on the lines suggested by Harder (1914) The presence of bacteria capable of decomposing sulphur bearing proteins and all compounds containing sulphur other than sulphates to sulphuretted hydrogen can be demonstrated by inoculating nutrient agar containing lead acetate and any one of the sulphur compounds with the Red Hills Lake water Four types of bacteria—a long spirillum with three to four windings, a vibrio, a bacillus and a coccus—were obtained (Dey and Ganapati, 1934) They were able to produce H_2S from sulphur, sulphites, thiosulphates and cystine but not from sulphate in Beijerinck's protein-free medium (Beijerinck, 1900) Moreover, none of these bacteria produced H_2S from Van Delden's (1904) liquid medium The presence of sulphate reducing bacteria in the lake has already been reported (Dey and Ganapati, 1934)

As for sulphur bacteria, the presence of the colourless one can be equally demonstrated by carrying out an experiment described by Winogradsky (Lafar, 1910, and Ellis, 1932) Purple coloured, sulphurless bacteria can be shown by inoculating Van Delden's medium with bits of rotting *Plumatella* collected from the raw water conduit and exposing the bottles to diffused light for a week A bean-shaped *Spirillum* almost agreeing with the description given by Molisch (1907) for *Rhodovibrio parvus* has been obtained

Purple coloured and green coloured sulphur bacteria have been isolated from the lake water making use of Van Niel's medium (1931)

Almost all the physiological groups of bacteria mentioned above are seen in the effluents or can be cultured from the slow sand filters at Kilpauk (see Chapter IV)

The bottom deposits at the Lake —The surface layer of the bottom sediment varies from yellowish to brown, but just beneath it the colour is black due to the presence of hydrated ferrous sulphide The black colour disappears on exposure to air Exactly similar conditions prevail in the slow sand filters at Kilpauk The top layer of the filtering medium is brownish and the lower portion is black due to iron sulphide The formation of black FeS is attributed to sulphate reduction (Dey and Ganapati, *l c*)

CHAPTER II

Biological Conditions of the Raw Water Conduit (7 5 miles long) from Red Hills Lake to the Water Works at Kilpauk

From Red Hills Lake the water flows by gravity to Kilpauk, a distance of 7 5 miles 57 ventilators are provided, the distance between two being about 1,000 ft They are arranged alternately as air inlets and air outlets The quality of the raw water was examined only once in 1926 from the sanitary view-point Samples drawn on the same day from a number of adjacent manholes yielded widely variant results, lactose fermentors varying from 'present in 1 c c to present in 60 c c ' (Ganapati, 1926) The entire conduit is water-tight, so that there is no possibility of any sub-soil water entering it (Hutton-Justice Committee Report, 1917-18, p 36)

Thick patches of brownish sponge-like growth are seen throughout on the floor and sides of the conduit just below the surface of the water They are found in abundance just near the ventilators This growth is *Plumatella Tanganyikae* (Rousselet) and is also reported to be present in the Water Works of Hamburg, Torquay and Colombo, and in the lakes Tanganyika, Nyassa, etc , in Africa (Dey and Ganapati, *l c*) Entangled in the meshes of this growth are numerous Infusors, Molluscs, Rotifers, Protozoa, Algae (*Pediastrum simplex* var *radians* Lemm , *Staurastrum* sp , *Pleurosigma* sp), *Beggiatoa* and small worms besides brown hydrated oxide of iron The decayed growth nearest to the walls of the conduit is always black The black portions on treatment with dilute hydrochloric acid evolve H_2S and become brown Exposure to the atmosphere turns it brown proving that the black colour is due to hydrated ferrous sulphide Similar black flakes of iron sulphide were noticed by Kolkwitz (1918) in the salt water ditches of Artern (Germany), beneath the surface of bunches of *Ruppia*, and he offered the explanation based on simple experiments that the process of oxygen consumption by aerobic bacteria took place on the surface, creating in the interior conditions favourable for anaerobiosis Hydrogen sulphide chiefly originated there 'by putrefaction and sulphate reduction, under the influence of the anaerobic fission fungi and led simultaneously to the formation of iron sulphide'

In the present case, the thick patches of the Polyzoa can be compared to bunches of *Ruppia* and the flow of water in the conduit must be considered slow as the fall from Red Hills to Kilpauk is 1 in 4600 A similar explanation for the formation of iron sulphide in the conduit suggests itself In order to prove that such was really the case, three bottles of 300 c c capacity were filled with raw water The first bottle was kept as control, to the second some decayed bryozoan growth was added, and to the third some growth, 0·5 gm of magnesium sulphate, and 0·1 gm of potassium phosphate All the three bottles were firmly stoppered, paraffined and kept in the dark for a fortnight. Within a week bottles II and III turned black, but the intensity was greater in the third bottle, which on being opened evolved a pure smell of sulphuretted hydrogen It is inferred that as a result of the decomposition of the added bryozoan growth the free oxygen of water disappeared first, whereby evidently favourable conditions for the multiplication of strictly anaerobic sulphate reducers originated, resulting in the production of hydrogen sulphide

Using Van Delden's medium (1904) Beijerinck's *Spirillum desulfuricans* (1895) has been cultured from a bit of decayed growth of the polyzoa By using methods similar to those mentioned at the end of the last chapter colourless and purple coloured sulphur bacteria and purple coloured sulphurless bacteria have been cultured

But a piece of filter paper soaked in alkaline lead acetate which was hung daily throughout the year 1929 did not turn brown or black on any occasion There was practically no production of free hydrogen sulphide in the conduit This helps us to decide that H_2S in the filtrates from the slow sand filters at Kilpauk is all produced during the process of actual filtration

Summary

(1) The water was found to vary bacteriologically when samples were taken on the same day at different places along the raw water conduit

(2) The artificial lead from the lake affords highly favourable conditions for the growth of Polyzoa containing several rotifers, infusors, molluscs, diatoms, bacteria and worms besides hydrated iron oxide Sulphate-reducing bacteria, colourless and purple coloured sulphur bacteria, purple coloured sulphurless bacteria, iron bacteria were cultured from decayed bits of the Polyzoa The inner portions of this animalcule are often black due to iron sulphide and an explanation has been offered that it is due to putrefaction and sulphate reduction Detached brownish and black pieces have often been found choking filter screens placed at inlets to the slow sand filters and on the surface of sand, at Kilpauk.

(3) It is free from 'free H_2S'.

CHAPTER III

The Quality of Raw Water prior to slow sand filtration.

'The character of the applied water has also much to do with the quality of the effluent independent of its bacterial content' (Turneaure and Russel,

1929) The chief characteristics of the raw water prior to slow sand filtration are briefly stated below:—

(*a*) ***Physical.***

There was no bad smell in the raw water prior to filtration at any time during the past twenty-five years As stated already, the colour and transparency varied in different seasons Suspended matter varied from time to time and was most profuse in the hot weather and south-west monsoon season This consisted essentially of polyzoan growths in various stages of decay, detaching themselves from the sides and bottom of the raw water conduit These bits were often found to choke the screens at the inlet chambers of the slow sand filters with the result that in course of time the screens were eaten away and holes appeared in them The object of placing the screens at the inlets to filter beds was thus frustrated. The screens were intended to prevent frogs, crabs, fish, etc , from entering the beds They damage the filtering skin formed on the surface of the sand filters

(*b*) ***Biological***

(i) Bacteriological quality Speaking generally, it may be stated that the raw water was of a fair quality almost throughout the year, lactose fermenters being absent in volumes of 60 c c to being present in 1 c c , and the average total colonies per c c varying between 500 to 1,500.

(ii) Phyto- and zoo-plankton found in the raw water at the Kilpauk end are·—

Volvocales

1 ***Eudorina*** sp
2 ***Phacotus lenticularis***, Ehrenb

Chlorococcales.

3 ***Oocystis*** sp$_1$
4. Do sp$_2$
5. Do. sp$_3$.
6. Do sp$_4$
7 Do. sp$_5$
8. ***Ankistrodesmus spiralis*** (Turner) Siemmr
9 Do sp nov
10 ***Kirchneriella lunaris*** (Kirchner) Möb
11. Do. do. var. nov.
12 Do. sp. nov.
13 ***Dictyosphaerium pulchellum*** Wood
14. ***Dimorphococcus lunatus*** A. Br.
15 ***Pediastrum clathratum*** (Schroter) Lemm.
16. Do ***duplex*** var ***cohaerens*** Bohlm

17 *Pediastrum simplex* (Meyen) Lemm
18 Do *simplex* var nov
19 Do *simplex* var *duodenarium* (Bailey) Rab
20 Do *sturmi* var *radians* Lemm
21 *Coelastrum cambricum* var *intermedium* (Bohlin) G S West
22 Do *microporum* Naegeli
23 Do *reticulatum* (Dangeard) Senn
24 *Scenedesmus perforatus* Lemm

Oedogoniales

25 *Oedogonium* sp

Conjugales

26 *Spirogyra* sp
27 *Mougeotia* sp

Desmidioideae.

28 *Closterium acerosum* (Shrank) Ehrenb
29 *Euastrum spinulosum* var *inermius* Norsdt
30 Do *cobulatum* var *tropicum* (W and G S West)
31 *Cosmarium Lundelli* var *corruptum*
32 Do *pseudo-connatum* var *ellipsoideum* (W and G S West)
33 *Staurastrum chaetoceras* (Schroder) comb nov
34 Do. *gracile* Ralfes
35 Do. *pentacerum* (Wolle) G M Smith
36 *Botryococcous Braunii* (Kütz)
37 Do *protuberans* W and G S West

Bacillariophyceae

38 *Melosira granulata* (Ehrb) Ralfs
39 *Synedra ulna* (Nitzsch) Ehrb
40 *Amphora* sp.
41. *Rhopalodia* sp
42 *Surirella robusta* var *splendida* (Ehrenb.) Heurck

Dinophyceae:

43 *Peridinium marchicum* Lemm
44. Do. *pusillum* (Penard) Lemm.

Euglenineae.

45 *Euglena acus* Ehrenb
46 *Trachelomonas* sp_2
47. Do. sp_3
48 Do sp_5

Cyanophyceae

49 *Microcystis elebens* (Kütz)
50 Do *flos-aquae* (Wittr) Kirchn
51 Do *marginata* (Menegh) Kütz
52 Do *robusta* (Clark) Nyggard
53 Do *scripta* (Richter) Geitler
54 *Aphanocapsa elachista*, var nov
55. *Aphanothece* sp nov
56 Do *nidulans* P Richt
57 *Gleocapsa calcarea* Tilden.
58 Do *magma* (Breb) Hollerbach
59 *Gleothece distans* Stizenb
60 *Chroococcus tenax* (Kirch) Hieron
61 *Gomphosphaeria aponina* (Kütz)
62 *Merismopedia glauca* (Ehrenb) Nag
63 Do *punctata* Meyen
64 *Tolypothrix* sp
65. *Anabaena sphaerica* Born
66. Do sp
67 *Spirulina laxissima* G S West
68 *Oscillatoria Raciborskii* (Woloez)
69. Do *limnetica* (Lemm)
70. Do *limosa* Ag
71. *Oscillatoria Tanganyikae* G S West
72 Do sp
73 *Lyngbya* sp
74 *Debris*

Zoo-plankton

Cladocera.

1 *Alonella karua* (King) Dad
2 Do *cambonei*

Copepoda

3 *Mesocyclops senckarti*

Ostracoda.

4 *Strandesia* sp.

Nematoda:

5 *Actinolaimus tripapillatus* (V Dady).
6. *Dorylaimus carteri* Bast

Fowler (1923) has stated that 'the case of vegetable growths, on the other hand, is by no means so simple, the products of polluting organic matter are food for lower forms of plant life and so it is possible for a reservoir to be practically free from pathogenic germs, and yet be green with microflora of different sorts This is the problem which has specially to be faced in this country (India) where the action of sunlight while fatal to bacteria stimulates photosynthesis . . . . ' 'It is this biochemical problem which those in charge of water purification works have got to handle in some form or other '

Chemical —Waring (1923) noticed intimate relationship between 'river-stage' and some of the important chemical constituents of Ohio river water Tastes and odours were noticed in public water supplies of Ohio State, and an attempt was made to find out if there was any correlation between the 'river-stage' and some of the important chemical constituents such as dissolved oxygen, absorbed oxygen, ammonia, alkalinity, turbidity, chloride and sulphate

The results of the weekly determinations during 12 months for the above constituents on the same plan as adopted by Waring (*l c*) are given in Table I.

(i) *Dissolved Oxygen* —Waring has stated that 'the decrease of dissolved oxygen constituent is the most important single factor entering into the intensity of earthy tastes and odours', for if no dissolved oxygen was present to oxidise readily the oxidisable organic matter present in raw water, then 'that oxidation must take place at the expense of certain reducing substances resulting in objectionable tastes and odours' A study of the results in Table I shows that there is a 'very high' positive correlation between 'lake level', and 'dissolved oxygen', the coefficient being +0 97 In other words, when the level of water in the lake went low, the dissolved oxygen also went low, and *vice versa* And when the level of water fell in the lake the production of sulphuretted hydrogen was found to be intense Estimations of dissolved oxygen were made by Winkler's method (1913)

So in the prefiltration water there is a decided diminution of oxygen when the lake level is low Therefore conditions for sulphate reduction are more favourable in the summer months

Again, the figures for 'dissolved oxygen' bear an intimate inverse relation to temperature of raw water, the Pearsons' coefficient being −0·96

(ii) *Absorbed Oxygen* —This test gives us a figure for the amount of oxygen absorbed by the organic matter This also shows that there is a 'very high' inverse correlation between the two, the Pearson's coefficient being −0·86

The results of a systematic study of the oxidisable organic matter of the raw water at the Kilpauk end made by Ganapati and Padmanabha Pillay (1936) during the years 1924–1934 showed:—

1 That the oxidisable organic matter had two maxima in a year, the first maximum occurring in the hot weather period; the second maximum

was in the south-west monsoon period. For the years 1930, 1931 and 1932, the first maximum was slightly higher than the second

2 That the lowest figure was reached in the north-east monsoon or cold weather period, when the lake level was highest

3 For the eleven year period the highest figure was reached in September, 1927 (drought year) and the lowest in December 1932 (maximum rainfall)

4 That a high negative correlation (Pearson's coefficient) of −0 693 was found between organic matter and lake level Regression of organic matter Y on lake level X is found to be linear by statistical tests The equation to the regression straight line is

$$Y = +0{\cdot}5427 - 0{\cdot}0062\,X$$

(iii) *Ammoniacal Nitrogen* —The annual averages varied from 0 001 to 0·006 parts per 100,000 during 1925–1935 (Ganapati), and according to Thresh (1913) indicates vegetable contamination

(iv) *Albuminoid Nitrogen* —This test indicates the ammonia produced by the decomposition of the nitrogenous organic matter by alkaline permanganate The results for 1929 show that there is a 'very high' inverse correlation between this and the lake level, the Pearson's coefficient being −0·78

(v) *Alkalinity* —These figures for 1929 bear a close relation to the plankton contents of raw water according to Whipple (1914) A study of the results in Table I shows that there is a 'very high' inverse correlation with lake level, the Pearson's coefficient being −0·76

(vi) *Turbidity* —This test fairly indicates 'the presence of particles of matter in suspension such as clay, silt, finely divided organic matter, and microscopic organisms' Estimations of 'turbidity' were made according to the U S Geological Survey Turbidity rod method (Whipple *et al*, *l c*) A study of the results (Table I) shows that there is no significant degree of relationship with the lake level, the Pearson's correlation coefficient being −0 07

(vii) *Chlorine*.—Table I shows that there is a 'very high' inverse correlation with the lake level, the Pearson's coefficient being −0·92

(viii) *Inorganic sulphate* 'SO_3' —Table I shows that there is a 'very high' inverse correlation with the lake level, the coefficient being −0·94

Further statistics for 1929 (Table I) show that there is a 'high' inverse correlation between 'dissolved oxygen' and 'absorbed oxygen', the coefficient being −0·74 and high direct correlation between 'sulphates' and 'absorbed oxygen', the coefficient being +0·80; while there is practically no significant degree of relationship between 'dissolved oxygen' and 'turbidity' and between 'turbidity' and 'absorbed oxygen', the coefficients being −0·074 and −0·013 respectively.

Summary and Conclusions of Chapter III.

(i) That there is a close relationship between the lake level on the one hand, and dissolved oxygen, absorbed oxygen, albuminoid nitrogen, alkalinity, chloride and sulphate on the other is known by their respective correlation coefficients There is practically no relation between the lake level and turbidity and between turbidity and absorbed oxygen There is 'high' correlation between dissolved oxygen and absorbed oxygen and between sulphate and absorbed oxygen

(ii) So in the hot weather and south-west monsoon periods there is excessive organic matter Oxygen content diminishes Temperature is higher Inorganic sulphates are fairly high H_2S producing bacteria are present Alkalinity is high and the stage is set for sulphate reduction with the resulting H_2S production and the attendant biological phenomena in the slow sand filters at Kilpauk

CHAPTER IV

Bio-chemical changes taking place in the Madras Slow Sand Filters

This chapter is considered below under (A) General, (B) Physical conditions, (C) Chemical conditions, and (D) Biological conditions

A *General*

1 *A description of the section of a Slow Sand Filter*

Briefly stated the sections of the filters beginning at the top are as follows —

Average depth of raw water	3' 9"
Fine sand	28"
Coarse sand	2"
Broken stone graded	4"
Brick under-drains	5"

(*a*) Average mechanical analysis of the fine sand layer is given below

Passed through	1/16	100%
Retained on	1/20	21·25%
,,	1/30	31·56%
,,	1/50	39·85%
,,	1/75	5·94%
,,	1/100	1·09%
Passed through	1/100	0·31%

(*b*) The uniformity coefficient of fine sand was 2 36

(*c*) Effective size of sand was 0·33 mm

2. *Life of the Slow Sand Filters and Filter Head.*

(*a*) The life of a slow sand filter is governed by the amorphous suspended matter and plankton in raw water In London 'the life of a slow sand filter varies from a week or even less to 3 months depending upon the season of the year and the condition of water' (Prescott, 1935) In Cheltenham, where the same system of filtration was adopted for twelve years, it was found that the life of a filter never exceeded three weeks (Pickering, 1934) At the Madras Water Works a filter bed worked for 86 days to 112 days at the very first run, but its second and subsequent runs were respectively reduced to about 20 days (G W F C R , 1930)

Section of a Slow Sand Filter, in Use at the Water Works, Madras.

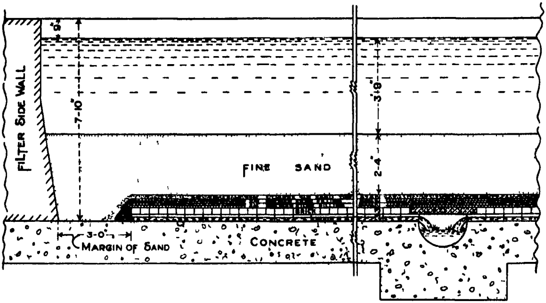


Fig. 2.

The life of a slow sand filter is only 2-3 weeks, and is also much less, i e 9–14 days in the hot weather and south-west monsoon periods, than in the other seasons of the year (Ganapati, 1926). The shortening of the life in the above periods has to be attributed to the excessive amount of organic matter in solution and in suspension.

3 *Penetration of Silt*

The depth to which silt penetrated into the sand layer is determined as follows. 'From each layer, one inch in depth, sufficient sand was taken to fill a glass cylinder three inches in diameter to a depth of three inches This was vigorously shaken with clean water and allowed to settle for half an hour, at the end of which period the depth of sediment over the sand was measured.' The results of a typical analysis in a Madras sand filter are as follows:—

Depth of layer from surface in inches	Depth of sediment after ½ hour settlment
0-1	1/2
1-2	3/8
2-3	1/4
3-4	3/16
4-5	3/16
5-6	1/8
6-7	Trace

'These figures show clearly that the colloidal matter penetrated to about 6" depth, in a slow sand filter with 28" thickness of sand ' (Madeley, 1923)

The silt was invariably dark brown, which on exposure became less dark or brownish

B *Physical Conditions of the Effluent*

(i) *Colour and Transparency* —During the hot weather and south-west monsoon periods the raw water was yellowish and opaque while the filtered water was colourless and clear except for the presence of floating whitish gelatinous particles of sulphur bacteria

(ii) *Smell* —The filtered water had a distinct smell of sulphuretted hydrogen This was not noticed in the very first run of a slow sand filter for two to three months but towards the end of the first run the smell was usually evident A new bed worked for a period of 50 days satisfactorily from 11th April, 1924, and had to be stopped on 31-5-34 for 4 days owing to the evolution of H_2S Another new bed worked for 47 days and then began to produce H_2S In the subsequent runs through the same filter beds the smell appeared much earlier (Ganapati, 1924)

The presence of H_2S gas was confirmed by lead paper test Sodium nitroprusside did not produce any reaction (Kenwood, 1920) in filtered water samples containing H_2S when a few drops were added, showing that H_2S and not Am_2S was liberated Glass beads soaked in isatin-sulphuric acid in a tube open at both ends and packed with glass wool did not produce the characteristic reaction for mercaptans (Lehmann and Neumann) when the tube was suspended in the filtered water chamber That H_2S and not Am_2S or mercaptans was produced in the slow sand filter effluents was established H_2S is noticed also in the slow sand filters of Adoni, Salem and Baroda, and this has been stated to be worse there during the summer months

Appreciable quantities of H_2S have been found near the bottom of lakes Mofford, Girote, Weissowo, Ritom, Hallurbo, and Hemmelsdorfer (Bavendamm, *l c.*) In all those places, the production of H_2S was attributed to sulphate reduction.

The presence of H_2S in the bottom layers of lakes Singetu and Hiruga, Japan, has been noted and its origin traced again to sulphate reduction by Yoshimura (1932).

Again, Ruttner (1932) has found H_2S in the hypolimnion of lakes in the East Indies, and ascribed its presence entirely to the activity of the sulphate-reducing bacteria

The odour of H_2S is often perceptible at the straining shaft of the Labugama lake in Ceylon (Hirst, 1921)

In Madras H_2S is noticed during the hot weather and south-west monsoon periods in the sewage-polluted Cooum river and Buckingham Canal

At Mettur, the third biggest artificial reservoir of the world, H_2S is evolved as the water escapes through the sluice gates

In all the places mentioned above the formation of the gas is ascribed to biological action Thresh *et al* (1933) have stated that 'in some cases hydrogen sulphide may be due to a purely chemical reaction but in many the more probable explanation is the decomposition of sulphates or of albuminous matter by low forms of vegetable life'.

In all the cases enumerated above (which is almost an exhaustive list) sulphuretted hydrogen is produced under natural conditions and was studied with reference to the presence of colourless and red sulphur bacteria The lakes of the temperate region referred to previously were not drawn on for domestic consumption and filtration with the aid of slow sand filters was not attempted so far as is known

In the tropics, however, in places which are not fed by rivers, water fit for human consumption is derived from artificial or natural lakes, *e g* Salem, Adoni and Madras The attempt to purify such waters by a system of slow sand filtration has the undesirable result of presenting in the filtered water an objectionable gas transmitted for human conception which was not found in the prefiltered water or at the source What would have been the result if the water from temperate lakes were so treated where the sulphate-reducing bacteria have been found must remain a matter for speculation All the necessary conditions for this trouble are there and the only varying factor is temperature.

Measures to get rid of this smell at Madras by pretreating the raw water for one year in 1929 with a dose of chlorine varying from 1 to 3 parts per million on the advice of Major Morrison (1920) were not successful (Ganapati, 1930)

(iii) *Temperature* —The temperature was noted for the influent and effluent of a slow sand filter This is shown in Table II There is no appreciable difference between the two This is also confirmed by the temperatures of the effluents collected from taps situated at different levels in a slow sand filter

C. *Chemical Conditions.*

The chemical changes which take place in the process of slow sand filtration of Red Hills Lake water have been studied by me and the Committees (G O. Nos. 1576, 546, 1934, 1550, 709, 932, 1419) appointed by the Madras Government from time to time The latter committees confined themselves to testing the effluent exclusively for its hygienic quality.

It is now proposed to discuss the chemical changes taking place in typical runs of filters under the following heads:—

I. *Dissolved Gases*
  - (*a*) Dissolved oxygen
  - (*b*) Free carbonic acid
  - (*c*) Sulphuretted hydrogen

II *Hydrogen ion concentration (pH)*

III *Estimation of electrolytes*
  - (*a*) Carbonates and bicarbonates
  - (*b*) Sulphates
  - (*c*) Chlorides
  - (*d*) Total Hardness
  - (*e*) Iron (Ferrous)

IV *Estimation of organic substances and their decomposition products*
  - (*a*) Oxygen absorbed
  - (*b*) Ammoniacal nitrogen
  - (*c*) Albuminoid ,,
  - (*d*) Nitrous ,,
  - (*e*) Nitric ,,

V *Discussion of results*
  - (*a*) Effect of slow sand filtration on dissolved gases
  - (*b*) Effect of slow sand filtration on organic matter (oxygen absorbed and ammoniacal N)
  - (*c*) Effect of slow sand filtration on sulphates
  - (*d*) Effect of slow sand filtration on chlorides
  - (*e*) Effect of slow sand filtration on total hardness.
  - (*f*) Effect of slow sand filtration on ferrous iron
  - (*g*) Effect of slow sand filtration on oxidised nitrogen

I (*a*) *Dissolved Oxygen*

Dissolved oxygen was estimated by the Rideal and Stewart's modification (1901) of the Winkler method Table III contains the results in two runs of an experimental slow sand filter containing three feet depth of fine sand. Four taps were located one below the other at different depths in the body of the filter Samples were collected on the first, third, eighth, tenth and nineteenth day in the first run, and on the second, fourth, eighth, and eleventh day in the second run

Vertical changes —In the first run, on the first day, dissolved oxygen was present in all the taps but there was a gradual fall from raw water to the final effluent. On the third day, the fall was more rapid from tap to tap than on the former occasion, and there was practically no oxygen in the last two taps Conditions were similar on the eighth day; and the fall was also greater On the tenth day, it was practically nil in the last three taps, the decrease from raw water to the final effluent reaching the maximum On the 19th day, the situation was the same as on the 9th day except for a slight increase in the effluent from the first tap.

Seasonal variations —The effluent from the first tap showed a day to day decrease It was 2 86 c c on the 1st, 1 69 c c per/l on the 3rd and 1 85 c c per/l on the 8th day, and 0·33 c.c /l on the 10th and 0·87 c c /l on the 19th day The dissolved oxygen was much less in the second tap and the fall from day to day was fairly great In the third and fourth taps a minimum amount detectable by the Winkler's test or nil was found on the different days

These results are confirmed in the second run. It is inferred therefore that the depletion of dissolved oxygen starts from the bottom of the filter and extends upwards, in about ten days anaerobic conditions appear to be formed in the entire body of the filter.

I (*b*) *Free Carbonic Acid*

Table III (*a*) contains the results of free carbonic acid examined at different depths in two typical runs of the experimental slow sand filter already referred to

Vertical changes —Free carbonic acid was not present at any time in the raw water, but it was present in the effluents drawn at all depths It gradually increased from the first to the last tap, the maximum and minimum being found in the last and the first taps respectively There was no significant difference from tap to tap

Seasonal changes —Though it was present on all the days in the first tap, the increase from day to day was not regular The results from the second run confirm the above findings

I (*c*) *Free Sulphuretted hydrogen.*

This gas was also produced The variations in the quantity of this gas from day to day are given in the Table below for a typical run

Table showing the quantity of H_2S produced in the final effluent during one run of Bed I

Date of starting.	Date of estimation	H_2S mg /L	Remarks.
13th July, 1929 ..	Started the filter.		
	July 16	0·6	....
	,, 19	1·0	....
	,, 22	1·3	....
	,, 25	1·5	....
	,, 28	2·0	....
	,, 31	2·6	....
	August 3	3·2	....

Stopped on August 5, 1929.

A gradual increase is noticed in the course of 19 days from 0·6 to 3·2 mg /l The Government Committee found in their experimental slow sand filter as much as 8·7 mg /l being the average of nine readings in October, 1929 The maximum recorded by them was 10 mg /l, and it was continuously present in increasing quantities (G O 932 P H , 12th April, 1930)

II *Hydrogen ion concentration (pH)*

In Table IV the pH values for raw and filtered water for the control slow sand filter for one typical long run is given It will be seen that while the pH value for prefiltration water varied from 8 2 to 8 4, that for the effluent decreased from 7·4 to 7·1

III *Estimation of Electrolytes*

(*a*) *Carbonates and Bicarbonates*

The typical changes taking place in the above substances is shown in Table V Carbonates were present in raw water but not in the effluents from the different taps This is due to the presence of free carbonic acid which converts the carbonates into bicarbonates

Vertical changes —The bicarbonates were higher in all the taps and on all days than the corresponding values for raw water The maximum difference was noticed between the raw water value and the first tap value, while the differences between successive taps were considerably less The differences between the second and third taps and between the third and fourth taps were not regular

Seasonal changes —The bicarbonate content in the first and second taps was not found to vary from day to day but was nearly constant, while in the third and fourth taps a distinct increase was noticed after 4 to 8 days

The increase in the first tap over raw water in its content of bicarbonate has to be attributed to the biochemical changes taking place on and below the filtering skin

(*b*) *Sulphates* (Table VI).

Estimations were made of the sulphate content of raw water and filtered water. From the latter, H_2S was removed by boiling after acidifying with HCl The results shown in Table VI indicate a loss in sulphate in the process of filtration, and the average loss in sulphate was 2 3 mg /l as SO_3 which corresponds to about 1·0 mg of H_2S per litre But the output of the gas (H_2S) is far in excess of what the loss (*i e* , the difference in the sulphate content of raw and filtered water) warrants The results shown in Table VII also confirm this The extra amount of hydrogen sulphide has to be explained (see pp. 260-261)

(*c*) *Chlorides.*

A perusal of the results in Table IV will show that there was no change during the process of filtration and so chlorides do not appear to have any biological significance.

(*d*) *Total Hardness*

There was no change in the total hardness as a result of slow sand filtration (*vide* Table IV)

(*e*) *Iron* (*Ferrous*)

Ferrous iron was absent in raw water, but was found in filtered water (Table IV)

IV *Estimation of organic substances and their decomposition products*

(*a*) *Oxygen absorbed*

Oxygen absorbed both by oxidisable organic matter and the inorganic matter (H_2S and ferrous iron) was estimated in the effluents from taps located at different depths of the small experimental slow sand filter (Tables VIII and IX) The vertical and day to day changes for the experimental sand filter are considered first

Vertical changes —With the increase in depth, the figures for oxygen absorbed (both for the 4 hours and 5 minutes test) increases Maximum figures are obtained in the final effluent

Day to day changes —Generally speaking, the results for both the tests show a definite increase

From Tables VIII and IX, it will be seen that the figures for oxygen absorbed were less than those of raw water until the appearance of H_2S and later on they increased

Seasonal changes —The seasonal changes for two years are shown in Table X Excepting January, February, November and December, the values for the effluent were always higher than the corresponding raw water values Maximum figures of 0·336 and 0·369 parts per 100,000 were obtained in September (south-west monsoon period) 1928 and 1929 respectively.

(*b*) *Ammoniacal N* (Table XI)

From Table XI for one typical bed, it will be seen that this figure showed a gradual increase from day to day and was always greater than the raw water figure This is never the case in all the sand filter effluents of the Metropolitan Water Board, London

It will also be seen that the figures for the effluent were equal to or very slightly greater than the corresponding raw water values in the north-east monsoon period (November and December) and in the cold weather period (January and February), while in the other months they were definitely higher than the raw water values In 1928 and 1929 the maximum figures were obtained in September (south-west monsoon period)

(*c*) *Albuminoid N* (Table XII)

While the former values were almost always higher than those of raw water, the albuminoid ammonia figures were always less than the raw water values.

(*d*) *and* (*e*) *Nitrous N and Nitric N* were both absent in the influent and effluent from all the slow sand filters (*vide* Table IV)

V (*a*) *Effect of slow sand filtration on dissolved gases*

Whipple *et al* (1929) have stated that 'when water containing a great deal of organic matter or plankton is filtered through slow sand filters oxidation of the decomposing organic matter may exhaust the supply of dissolved oxygen' Noll (1929) found that the dissolved oxygen content of water changed in passing through sand filters and stated that oxygen might have been used up either by bacteria or by chemical reaction in the filters Raghavachari and Ganapati (1929) have found that in the Madras slow sand filters 'there was a consistent and progressive reduction in the oxygen content from day to day and that when sulphuretted hydrogen appeared in the filtrate, the dissolved oxygen figure showed further progressing reduction and finally reached zero as the hydrogen sulphide increased considerably' The results obtained in the present case are in agreement with those of Whipple (*l c*) and Noll (*l c*) The depletion of 'dissolved oxygen' may therefore be due to bacterial decomposition of organic matter creating anaerobic conditions inside the filter

V (*b*) *Effect of slow sand filtration on organic matter* (*oxygen absorbed and ammoniacal N*)

This conclusion is further supported by the increased figures in 'free ammonia' and the low figures for 'albuminoid nitrogen' and the presence of sulphuretted hydrogen in the filtered water Ammonia and hydrogen sulphide might have resulted from the decomposition of sulphur-bearing proteins contained in the bodies of planktons, Infusoria, algae, Crustacea, Bryozoa, etc , brought in by raw water and deposited in the filter sand The three gases hydrogen sulphide, carbon dioxide and ammonia are characteristic products of such a process (Lafar, 1910 ; Singer, 1930) The decrease in pH of filtered water may be due to the presence of hydrogen sulphide and carbon dioxide

The results of free carbon dioxide, pH 'fixed solids', 'ignitible matter', 'ammonias' and 'absorbed oxygen' are shown in Table XIII A study of the results shows (i) that hydrogen sulphide was noticed on the fourth day of the starting of the filter, (ii) increased figures for 'ammoniacal nitrogen', and 'absorbed oxygen', and (iii) decreased figures for 'albuminoid nitrogen' were noticed in the filtrates Further, while there was no free carbon dioxide in the raw water, the filtered water samples showed a distinct increase There was an average loss of 1·56 parts per 100,000 of 'ignitible matter' in the process of filtration. (This result is probably high as errors may arise [Notter and Firth, 1921] in the form of loss of water of crystallisation from calcium sulphate and from decomposition of carbonates)

From Tables IV and XIII it will be evident that decomposition of organic matter is taking place in the filter resulting in the production of 'free ammonia' and carbon dioxide. Hydrogen sulphide is also produced at the same time and it has to be examined whether this gas is the direct result of decomposition of organic matter as 'free ammonia' and carbon dioxide or by any other process, or both (Thresh *et al*, 1933, Harder, 1919) The high figures in the two cases of 'free ammonia' and 'absorbed oxygen' may be due to the influence of hydrogen sulphide, for, in the determination with Nessler solution of 'free ammonia', the intensity of colour is increased by the presence of this gas Due allowance was not made for this The figures for absorbed oxygen are also similarly exaggerated For Thresh *et al* (1933) have observed that 'inorganic substances like the lower oxides of iron, nitrites and hydrogen sulphide are capable of absorbing oxygen from potassium permanganate' (used in Tidy's 4 hours' test) and therefore have suggested in such cases a method of estimating the amount of oxygen taken up by these substances

Table XIV contains the results of analysis for 'ammonias' and 'absorbed oxygen' in Bed I Error arising from the presence of sulphuretted hydrogen in the filtered water in each case was also determined, the former by the method described by Desgrez, Lescoener and Manjean (1926) and the latter according to Thresh's method (1933) From the results, the following observations appear justifiable·—

(i) There was a distinct increase of 'free ammonia' in the filtered water

(ii) An appreciable amount of 'free ammonia' was still found in samples of filtered water from which hydrogen sulphide was removed

(iii) There was a distinct decrease in the figures for 'albuminoid nitrogen'

(iv) The figures for 'total oxygen absorbed' (by organic matter and hydrogen sulphide) were higher than the corresponding figures for raw water

(v) But the figures for 'oxygen absorbed' by hydrogen sulphide alone showed a gradual increase

(vi) The figures for 'oxygen absorbed' by organic matter alone (difference of figures in columns 13 and 14) were lower than the corresponding figures for raw water

From the foregoing it may be concluded that there is an appreciable quantity of 'free ammonia' corrected for hydrogen sulphide in the filtrates and that 'oxygen absorbed' by organic matter is much less in the filtrates

Statistical correlations

The figures for the first run in Table XIV show that there is 'high' and direct correlation between 'ammoniacal nitrogen' (not corrected for hydrogen sulphide) on the one hand and 'total oxygen absorbed' and 'oxygen absorbed' by sulphuretted hydrogen on the other hand, the coefficients being +0 86 and +0·90 respectively There is also a very high and direct correlation between 'total oxygen absorbed' and 'oxygen absorbed' by hydrogen sulphide, the coefficient being +0 97 and between organic matter lost in the process of filtration (being the difference in figures between 'oxygen absorbed' by organic matter alone in raw and filtered water) on the one hand and hydrogen sulphide and 'ammoniacal nitrogen' (corrected for hydrogen sulphide) on the other, the coefficients being +0·60 and +0·44 respectively. Therefore, it is established that a close relationship exists between organic matter lost in filtration and hydrogen sulphide and 'free ammonia' noticed in the filtrates.

V (*c*) *Effect of slow sand filtration on the sulphates*

Is the production of hydrogen sulphide of organic or inorganic origin or both?

The next point to consider is about the origin of H_2S. It has already been shown in the Table on p. 254 that (i) a gradual increase in H_2S is noticed as a filter goes on working and that in the course of one week the gas was found to increase from 0·6 to 3·2 mg. per litre, (ii) a loss in sulphate content occurs in the process of filtration which corresponded to 0·8 mg. per litre, and (iii) the output of H_2S was far in excess of what the loss (*i.e.* the difference in the sulphate content of raw and filtered water) warrants. The extra amount of H_2S has to be explained and only two other sources naturally suggest themselves. One of them is the sulphur-bearing protein in organic matter of raw water.

Estimation of sulphur-bearing proteins

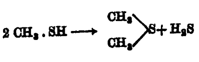
The total sulphates were estimated as described below[1] and the inorganic sulphate as stated in Scott's. The difference between the 'total sulphates' and 'inorganic sulphate' gives the figure for sulphur existing in other forms of combination (sulphur-bearing proteins). The results are shown in Table XV. A study of the results shows that there is not an appreciable difference in the two cases in raw water samples. Within the limits of experimental error they appear to be the same, and as such it is quite probable that there is no appreciable amount of sulphur-bearing proteins, which could be estimated in samples of one litre. This conclusion is supported by Peterson, Fred and Domogalla's (1925) study of the Wisconsin lakes for the presence of amino-acids such as tryptophane, cystine, histidine and tyrosine.

Cystine [2], the sulphur containing amino-acid, varied from 1·5 to 7·6 mg. per cubic metre in the different lakes and in one lake the surface sample

---

[1] One litre of water was evaporated to dryness over a water-bath and the residue was treated with fuming HNO_3 and transferred to a flask fitted with a reflex condenser. The flask was heated over a water-bath for three hours. Then the contents of the flask were transferred to a porcelain dish and HNO_3 was driven off by evaporating twice nearly to dryness on the water-bath after adding HCl, the sulphate was then estimated as in the case of inorganic sulphate (Scott).

[2] Cystine is the sulphur containing amino-acid from which the putrefactive bacteria produce H_2S (Wilson) probably in the following manner. The decomposition of Cystine leads through thioglycolic or thiolactic acids to mercaptans which are further changed into H_2S.



$$2\,CH_3.SH \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!S + H_2S$$

contained much less than the bottom sample The Red Hills Lake water drawn as it is from near the surface does not contain appreciable quantities of sulphur bearing proteins In comparison with inorganic sulphate, organic sulphur is insignificant, and as such this source of sulphur at the filter may be considered negligible The only other source is sulphate from sand

The contribution of sand in filter beds to the amount of sulphate available for reduction and its rôle in the evolution of H_2S

Table XVI shows the result of analysis for iron and sulphate of different samples of sand (i) fresh river sand, (ii) used and washed sand (from Filter No 1), and (iii) used but not washed black sand (from the same filter) The sand used in the filter and unwashed contains more iron and sulphate than the sand used in a filter but washed (In practice the same sand is washed and used in the filter every time a filter goes out of action) Iron in fresh river sand (the sand used in the filter was also obtained from the same place) was very much the same as the used and washed sand Therefore it appears that sand as it is being used in filters gathers to itself more and more of iron and sulphate The process of such accretion is explained

It has been said that the soil beneath the lake is laterite in origin and rich in iron Iron in the form of brown ferric hydroxide is brought from the lake and deposited in sand, especially in summer months

H_2S produced by sulphate reduction goes to form iron sulphide which later when exposed to the sun and air for purposes of cleaning becomes its sulphate (Van Hise) Thus the amount of sulphate in sand is augmented and is never diminished

The sand in the beds has been used for several years and the original sulphate if any must have gone the way of other inorganic sulphates, and what is now found in the sand is probably the newly formed sulphate deriving the sulphur for its formation from H_2S obtained chiefly by sulphate reduction

The two Tables XV and XVI clearly show (1) that H_2S from sulphur containing proteins is negligible when compared to sulphur from inorganic sulphates, (2) that the sand in the beds, after it has been long in use, does not of itself contribute sulphur

There still remains the problem from where the H_2S comes, in excess of what the loss in sulphate as a result of reduction warrants us to expect.

What is the agency that controls the increased output of H_2S?

The controlling agent in all probability is carbon dioxide

Decomposition of protein matter liberates chiefly CO_2 and free ammonia and also some H_2S The process of decomposition is most vigorous in the summer months when concentration of organic matter is the greatest and the temperature is most favourable.

The sulphide of iron however formed, but observed in large quantities in sand used in filters, is acted upon by CO_2 and water (Lipman, 1921). When sufficient carbon dioxide is formed alkaline conditions may change into acid conditions at some stage inside the filter Under such conditions the sulphide of iron which is only slightly ionised under alkaline conditions would be converted into H_2S, while the sulphides of Ca and Mg are easily acted upon by CO_2 and water resulting in H_2S according to the following equation —

$MS+CO_2+H_2O \longrightarrow H_2S+MCO_3$ where M stands for Fe, Ca and Mg (Harder, *l c*)

Einsele (1936) has stated that in lakes 'Sicher ist dabei bis jetzt nur das eine daβ die Reaktion

$FeS+H_2CO_3 \longrightarrow FeHCO_3+H_2S$ under allen Umstanden sehr langsam vor sich geht'

It has been noticed in Table XIV that an increased output of H_2S is always accompanied by an increased production of 'free ammonia' There can be no direct correlation between H_2S and 'free ammonia', but the apparent relation as revealed in that table only shows that the increased amount of 'free ammonia' is accompanied by increased quantities of CO_2 resulting in a corresponding increase of H_2S

In the winter months the output of H_2S is very much less The process of sulphate reduction takes place even in those months as evidenced by the formation of black iron sulphide in sand but H_2S is not noticed in the filtrates in the same large quantities as in summer This is due (1) to the small scale of decomposition of protein matter as a result of dilution of organic content in the lake, and (2) to H_2S being taken up by iron in sand to form black iron sulphide

It will be seen therefore that sand acts only as a storehouse for the sulphide and CO_2 as the regulator of the output of H_2S in slow sand filters In other words, more CO_2 production means more H_2S production So the increased output of H_2S is thus explained

Agency responsible for H_2S formation

The chief source of sulphur appears to be inorganic sulphate in raw water It is, therefore, suggested that 'Sulphate Reducers' are the active agencies responsible for the reduction of sulphate to H_2S in sand filters, while the putrefactive bacteria play but a secondary rôle in the production of this substance from sulphur-bearing proteins Beijerinck's ***Spirillum desulfuricans***, the sulphate-reducing organism, has been isolated from the lake water, conduit and the sand filters by me (Dey and Ganapati, *l c*) and it has been proved that the biological reduction of sulphate is the major process responsible for the production of H_2S in the sand filters.

V (*d*), (*e*) ***Effect of slow sand filtration on chlorides and total hardness*** (Table IV)

No change is seen in the above as a result of slow sand filtration.

V (*f*) *Effect of slow sand filtration on ferrous iron* (Table IV)

The iron content increases in the filtered water and this has to be attributed to the excessive amount of free carbonic acid formed inside Carbonic acid converts iron compounds into soluble ferrous carbonate and carries them away in solution.

V (*g*) *Effect of slow sand filtration on oxidised nitrogen* (nitrites and nitrates)

Whipple *et al* (1927) have stated that as a result of oxidation the effluent of slow sand filters usually contains a large amount of nitrates Raju (1925-26) has stated that according to some people the efficiency of filtration 'in the case of slow sand filters is at least partly due to the activity of the nitrifying organisms establishing themselves on the sand surface', and he tried to find out how far the above statement was true in the case of Bengal filters He found that 'to all appearance the surface of slow sand filters appears to be an ideal place for the vigorous development of the nitrifying organisms but the results obtained in the course of this investigation do not at all point to any such action' The results obtained at Madras seem to confirm Raju's findings, for at no time have nitrites or nitrates been detected in the effluent from slow sand filters More of this under 'nitrifying organisms' has been given

Summary and Conclusions

I *Dissolved gases*

(*a*) Dissolved oxygen is reduced almost completely

(*b*) Free carbonic acid is increased

(*c*) Sulphuretted hydrogen is increased gradually.

II *Hydrogen ion concentration (pH)*

pH is lowered and reaches round about the neutral point.

III *Electrolytes.*

(*a*) Carbonates are absent and bicarbonates show a definite increase.

(*b*) Sulphates are reduced to an appreciable extent due to biological action of Beijerinck's *Spirillum desulfuricans*

(*c*) Chlorides are unaffected

(*d*) No change in total hardness.

(*e*) There is a definite increase in ferrous iron in the south-west monsoon period.

IV *Organic substances and their decomposition products.*

(1) In one litre of raw water, sulphur-bearing proteins are negligible.

(2) Oxidisable organic matter figures are always higher than the corresponding raw water figures when H_2S and ferrous iron are present. But if due

allowance is made for the latter, then the absorbed oxygen figures are considerably lower than those for raw water. A maximum reduction of about 60% is noticed

(3) Ammoniacal nitrogen figures also show similar high figures like (2) and the presence of H_2S is responsible to a large extent for this increase Estimations made after removing H_2S also give higher figures than those for raw water

(4) Albuminoid nitrogen always shows a reduction over raw water, the average reduction being about 50% in the hot weather and south-west monsoon periods

V How the filter sand acts only as a storehouse for the sulphides, carbonic acid most probably regulates the output of free hydrogen sulphide in the filtered water, and how the various other changes mentioned in I to IV are brought about in a slow sand filter have been explained

D *Biological Conditions*

The Madras slow sand filters are able to remove the visible suspended matter causing turbidity but are unable to retain all the bacteria in the crude water In Germany sand filters are said to remove about 99% of the total number of bacteria present in raw water (Rideal and Rideal, 1914), and again at Albany and Washington, 99 6% (Turneaure and Russel, 1929)

The bacterial efficiency of the Madras slow sand filters is considered below under the following heads —

A Tests employed for determining bacterial efficiency

B A consideration of the bacteriological results of the sand filters (i) run under ideal large scale working conditions by the Corporation and (ii) run under ideal conditions on a small scale by the Government Water Filtration Committee at Kilpauk separately and using one of the Corporation filters.

C Special investigations.

D Discussion of results

A *Tests employed for determining bacterial efficiency of a purification plant*

Two tests are usually employed for determining the bacterial efficiency of a purification process They are · (i) the total colonies count per c c on nutrient agar or gelatin and (ii) *B Coli* content As for the first test, the estimation of the total colonies count of the water before and after filtration is generally employed for assessing the degree of bacterial purification effected in the course of filtration. Raju (1926-27) abandons this as he thinks it is subject to considerable experimental errors and is in favour of *B. Coli* estimation with Macconkey's bile-salt-neutral-red-lactose broth using varying quantities of water. He concludes from the dry weather results of slow sand filters of Hooghly-Chinsurah water works that filtrates should conform to a minimum standard of no lactose fermenters in 10 c c of water (Raju, *l c*) He has employed this test for assessing the bacterial efficiency of Bengal sand filters Whereas in Europe (Rideal and Rideal, 1914) and America (Turneaure and Russel, 1929) prominence is given to both the tests and according to the first test 99 6 per cent of the total bacteria are to be retained by the sand filters Raju (*l c*) states that for European countries filtered waters should not contain *B Coli* in 50 c c of water and that the total count per c c should not exceed 100 *B Coli* per cent positive in 1 c c (being less than 1%) is used as an index Sir A C Houston considered results with 100 c c of samples most satisfactory A P H A standard (1933, p 145) has recommended only *B Coli* test 'The omission of plate counts from the standard is not to be construed, however, as denying or minimising their importance in routine examination made in connection with the control of purification processes'

Considerable data have been collected during the past 25 years regarding the bacterial efficiency of the Madras slow sand filters The previous investigations have yielded considerable interesting information on which the present paper has been partly based

B (i) *The bacterial efficiency of a slow sand filter worked under ideal conditions* (G O No 1934, L & M, 1st Sept, 1923)

(Bed I, one of the Madras Corporation Filters, was worked under 'ideal' conditions by the Government Water Filtration Committee)

The Committee stated 'Before definitely condemning this method for the Madras Water Supply it was considered advisable, therefore, to obtain one of the filter beds for the purpose of testing its capacities under ideal conditions This bed (Bed No I) was overhauled, disinfected, and relaid and has been worked under the most carefully controlled conditions The results obtained are of the utmost importance The bed commenced work on 14th January 1923 and ran with satisfactory results until 16th March 1923'

The bacteriological results (p 26, G O No 1934, L. & M, 1st Sept, 1923) of this experiment are summarised in the table below

Bacteriological results of Filter Bed No I run under ideally controlled conditions by the Govt. Water Filtration Committee in 1923 (vide p. 26, G O. No 1934, L. & M., 1st September, 1923).

Period of run.	Description of samples	No of samples	Average T C./c.c	−60 c c	60 c c	20 c.c	10 c c	5 c c	1
14-1-23 to 16-3-23	Raw water.	18	1865		.	2	1	12	3
	Bed I	18	987		11	2	2	2	1

From the above table the per cent reduction of total colonies count per c c works to 47·9% and the 'satisfactory' results (±60 c c) were shown in 61·1% of the samples collected The time that was taken to give the first 'satisfactory' effluent was 15 days (29-1-23)

In the next table the performance of the sand filter as worked ordinarily during (1914–1923) is compared with that of Bed I run under ideally controlled conditions

Period	Per cent reduction of total colonies count per c c	Most 'satisfactory' results (±60 c c.)	Least 'satisfactory' results (1 c c.).
1917 to 1923	69 7	19 6	9 3
14 1-23 to 16 3 23	47 9	61 1	5 5

The bacteriological results of Bed I have been considered 'satisfactory' when only 47·9% of the total counts were removed and when 61·1% of the samples alone were 'satisfactory' according to the Committee's standard The results do not at all approach those obtained by the European and American slow sand filters Elimination of the total bacteria to the extent of 99 9% have been obtained in Europe and America If this is the best that is possible bacteriologically under 'ideal' conditions, slow sand filtration at Madras should be considered a failure More is to follow In the words of the Committee 'This experiment is of the utmost importance, for it proves that simple slow sand filtration (from vertical inches per hour) with the Madras water cannot be carried on without the formation of H_2S no matter how carefully the process of filtration is controlled It is possible that the production of H_2S can be correlated with a definite range of temperature This, however, is more of scientific than of practical interest The formation of this disagreeable gas is sufficient to condemn the process of purification which is responsible for its production All the available evidence so far produced shows that slow sand filtration by itself is not able to produce a potable water Some other means of purification must therefore be sought' (p 5, G O No. 1934, L & M , dated 1st Sept., 1923) Further comment would appear needless regarding the bacterial efficiency of Madras sand filters

(ii) *Seasonal Variations in Bacteriological Results.*

The Committee experimented with a small filter of 7,200 gallons daily filtering capacity designed on the lines of the Madras filters but with the following important differences. The depth of fine sand in this filter was kept constant at 36″ and the depth of water was also kept constant at 3 ft.

The bacteriological results of this filter for the different seasons for a period of two years are shown in the table below.

Per cent reduction of Total counts per c c (calculated from G O No 1550 *P H*, *2nd August*, 1928, *G O No* 709 *P H*, *15th March*, 1929, *and G O No* 932 *P H*, *12th March*, 1930)

Year	Cold Weather			Hot Weather			S W Monsoon			N E Monsoon	
	R W	S S F	Per cent reduct	R W	S S F	Per cent reduct	R W	S S F	Per cent reduct	R W	S S F
1927 (two months)										3,240	673
1928	2,253	327	85 5	2,888	521	81 9	2,461	629	74 4	3,925	748
1929	2,550	393	84 6	2,627	242	90 7	3,694	559	84 8	3,696	287
Average			85 0			86 3			79 6		

From the above table it will be seen that (i) there is not much difference in the per cent reduction of the total bacterial count from season to season, the difference between the maximum and minimum being only about 5%, (ii) the maximum per cent reduction was in the hot weather (86 3%) and the minimum in the south-west monsoon period, (iii) the per cent reduction obtained in this experimental filter is far greater than that obtained ordinarily in the Madras filters , (iv) these results do not approach the European and American standard of efficiency even under the best conditions on an experimental scale Raju (*l c*) found from his study of the slow sand filters in the Hooghly-Chinsurah Water Works that dry weather samples (September to April) reached a much higher degree of purity (82%) than those examined in monsoon months (June, July and August) (The division of weather condition in Bengal appears to be different from those adopted by the All-India Meteorological Department)

C *Special Investigations*

(*a*) ***Experiments on artificial filming by alum.***

One of the troubles with slow sand filters in the tropics is that when the water is comparatively clear as a result of long storage or only contains colloidal organic matter in fine suspension it takes a long time to form a filter skin and the filters settle down to long runs without the filter head increasing to more than 2″ or 3″. In such cases the sand filters give poor bacteriological results probably due to organic matter in solution or in colloidal form penetrating into the lower layers of the filter Buswell (1928) has stated that 'where this type of filter is still in use alum is now generally employed instead of depending on the naturally formed film In the case of the Madras slow sand filters, one of the Govt Committees (1917) stated that the poor bacteriological results were probably due to the inefficient formation of the filtering skin on the surface of sand, and this was made apparent by the filter head remaining constant at 2″ or 3″ for months So to quicken the formation of the slimy layer, alum was added to the raw water Water was let in and alum solution added before starting the filter Alum was added at the commencement and some more alum after 7 or 10 days only where necessary, that is to say, a second treatment was resorted to only when the formation of the skin was not sufficiently aided by the first treatment

Filter Beds 1, 4, 6 and 9 were treated in the manner described above and the results of the bacteriological examination and other connected data are given in the table below

Period of runs	No of runs	No of samples	Bed No	Raw water		Filtered water Lactose fermenters in						Average total count per c c on nutrient agar at 37 C after 48 hrs
				L F in 5 c c	T C per c c	— 60	60	20	10	5	1	
22-7-24 to 2-11-24	4	25	IX					8	10	7		480
31-7 24 to 2-11-24	4	8	I				1	2	1	4		480
8-7-24 to 22-7-24	1	6	IV						3	3		698
25-7-24 to 7-11-24	3	25	VI				1	2	9	13		518
Average				73%	991							544

The following conclusions are arrived at from the above table —

1 That only 2 out of 64 samples, *i e* 3 1% of the samples alone can be classed as 'satisfactory' according to the standard for *B Coli* adopted by the Govt Water Filtration Committee

2 The Filter was able to effect a reduction of 45 1% only in the test for total colonies count

Table showing the treatment given to beds on artificial filming slow sand filters

Started on	Stopped on	Life of the sand filter at 4" rate	Treatment given to the bed
8-7-24	22-7-24	Bed No 4 9 days	1" sand 200 lbs alum.
25-7-24	31 8-24	Bed No 6 34 days	Completely overhauled and 200 lbs of alum used.
5-9-24	11-10-24	29 ,,	1" sand and 150 lbs alum
16-10-24	17-11-24	16 ,,	1" sand and 186 lbs. alum
22-7-24	13-8-24	Bed No 9 20 days	1" sand dug to about 9" depth and used 200 lbs alum
17-8-24	5-9-24	15 ,,	1" sand dug to 6" depth and put in 1" washed sand and used 200 lbs alum
10-9-24	6 10-24	22 ,,	Removed 1" sand and replaced 1" washed sand and used 2 cwt. of alum.
11-10-24	1-11-24	17 ,,	Removed 1" and put in 1" washed sand—no alum.

The performance of the sand filters by this process cannot therefore be considered as efficient.

C (*b*) *Experiments using chlorinated raw water for the sand filters*

Major Morrison (G O No 546 M , 1920) had stated that chlorination at Red Hills would offer a definite solution for the Madras problem This was tried in 1926-27 at Red Hills and later at Kilpauk itself at a point where the chlorinated raw water would take about ten minutes to reach the filters Even after the application of chlorinated raw water the sand filters gave poor bacteriological results, and a special investigation was made in 1929 to elucidate the probable causes for the poor results (Ganapati, 1929)

D *Discussion of Results*

(i) *Reasons for the poor Bacteriological results in the Madras slow sand filters*

(1) A constant level of water over sand is not maintained but the level is varied from day to day, as there appears to be some engineering difficulties in the way of maintaining a constant level

(2) *Thickness of sand.*—'The original depth of sand must be sufficient to form an effective filter and besides to allow of several scrapings without the renewal of the sand Inasmuch as the bacterial efficiency depends in part on the action which takes place in the body of the filter and not exclusively at the surface, an increase in depth within certain limits will tend to increase the efficiency of the filter The effect of deep beds is similar to that of fine sand in steadying the action of a filter, and it has been clearly shown by the Lawrence Experiments that the operation of beds 4 to 5 ft thick is not so much affected as that of beds 1 to 2 ft thick by such disturbance as variations in rate, scraping of beds, etc , although the results with perfectly uniform conditions are not materially different The effect of depth is also very much important in causing a more uniform action over the entire bed of a freshly cleaned filter by minimising the effect of frictional resistence in the underdrains ' (Turneaure and Russel, *l c*)

For the foregoing reasons the minimum thickness should be about 2 ft and the maximum 3 to 4 ft But the depth of sand in individual Corporation beds varied from 9" to 24" which might have accounted partly for the poor bacteriological results though the uniformity coefficient of sand was between 2 and 2·5 and effective size was between 0·2 to 0·4 mm

(3) The water used to feed a bed about to start was of poor quality being derived from the indifferent mixture of filtrates Further, it is well known that in many cases there is a considerable decrease in the bacterial efficiency of a filter for some time after scraping and refilling with sand and it is the usual practice to waste the effluent for a day or two or the filtration is begun very slowly. The filters are started in practice with this initial disadvantage The filtrate during the first few days was always bacteriologically much poorer in quality than the filtrates obtained afterwards Madeley (1918) found that

efficient filtration did not start for about 16 days in the case of both covered and uncovered filters and that the total counts of bacteria and the numbers of lactose fermenters were both greater in the filtered water than in the unfiltered

(4) To secure efficient and reliable results a filter must be operated with gradual increase in rate Violent changes in rate cause ruptures in the filtering skin A considerable depth of sand serves to steady the action But at Madras a bed was brought up to its maximum rate of filtration which was variable from 4" to 8" vertical per hour sometimes even within 24 hours So the beds did not get a chance to form an efficient film before their effluents were drawn into the main

The Madras plant designed to operate at a slow rate of 4" vertical per hour was in practice converted into a semi-slow sand plant due to inadequacy of sufficient filter beds, or rather a plant with no fixed rate of filtration, resulting in an unsatisfactory filtrate for the town supply So much for the practice which obtained at Kilpauk Water Works

The experimental filter, however, showed that slow-sand filters should give better results if the practice was more in accordance with the theory of slow sand filtration This will be true with the qualification and it is a very important qualification that if H_2S did not result in the actual process of slow sand filtration due to sulphate reduction by bacteria under anaerobic conditions But the sand filters almost always creates optimum conditions for sulphate reduction The bacterial efficiency of slow sand filters is granted and fully borne in mind when it is stated in these and other pages that slow sand filtration is unsuited for the tropics A solution is sought in the direction of rapid sand filters which do not afford anaerobic conditions Whether this ideal condition will be achieved with the help of mechanical filters (rapid filters) or by a modification of the plant at Kilpauk I prefer to leave open here.

Algal Growth in Sand Filters

(ii) *Algae in the Sand Filters*

The surface of sand can be compared to a lake or reservoir bottom where dead algae settle and decompose So when raw water containing plenty of algal cells are filtered through sand filters, the algae are retained mostly on the surface of the sand and this constitutes the 'vital layer' According to Kemma (Whipple *et al*, 1927) the organisms are found in three conditions: (i) forming the vital layer or schlammdecke, (ii) attached to the walls of the sand filters, and (iii) floating free in water Organisms in the three states have been examined from time to time and the important ones in each state are given below:

Organisms in the vital layer are:—

1. *Oscillatoria limnetica*
2. „ sp.

3 *Peridinium Marchicum*
4 *Oocystis* spp
5 *Aphanocapsca elachista* var nov
6 *Microcystis scripta*
7 „ *robusta*
8 *Navicula* sp
9 Gnat worms

Attached to the sides are —

1 *Scytonema* sp
2 *Tolypothrix* sp
3 *Oscillatoria* sp
4 Gnat worms

Free floating organisms vide pages 244–246

(iii) *Vital Layer or Schmutzdecke*

That the chief agent in effective filtration is the vital layer formed at the surface of a slow sand filter is the view held by the German School (Turneaure and Russel, *l c*) The vital layer is composed of an upper 'gelatinous semi-colloidal partially organised layer strengthened by a net work of algae' and a lower 'stratum of decomposing organic matter underlying sand' It is in this lower portion that saprophytic organisms 'split up the complex albuminoid ammonia into their simpler substances' and lower down nitrifying bacteria are found which thrive upon the ammonia, nitrites, etc , supplied from above For the oxidation of the above substances, the nitrifying bacteria are supplied with oxygen by photo-synthetic activity of chlorophyll bearing organisms which have collected on the surface of the sand layer The vital layer as a whole effects 'not only a removal of organisms by adherence to the film but also a decrease in the nitrogenous organic content as measured by albuminoid ammonia and nearly corresponding increase in the nitrate' (Turneaure and Russel, *l c*). According to some people the efficiency of filtration is at least partly due to the activity of nitrifying organisms establishing themselves on the surface of sand (Raju, 1924-25)

But the American school (Turneaure and Russel, *l c.*) does not attach the same importance to the formation of the upper portion of the vital layer. Americans have noticed in their experiments that in a brief time an organic slimy deposit in the sand is formed by bacterial growth and that this deposit adds to the efficiency of the filters even with raw water of low turbidity This deposit is not quite the 'skin' spoken of previously but its action is very much similar. At Bedford non-submerged percolating filters are in use This slimy deposit is formed in those filters and the efficiency of the filter is considered to be largely due to it. The non-submerged percolating filters experimented with by the Water Filtration Committee, Madras (1928, 1929, 1930, and 1931) have also given good results and it would appear that the slimy deposit serves very much the same purpose that the vital layer serves in the case of submerged slow sand filters

Let us consider the case at Madras Madeley (1918) has described this in detail 'The filtering layer consists of two distinct portions which play a definite rôle in effecting purification The top portion is the sedimentary skin forming on the surface of the sand, which corresponds to the upper portion of the vital layer described above and consists of suspended matter both organic and inorganic The thickness and colour of the 'sedimentary skin' depends upon the amount of suspended matter present in the water During the hot weather and the south-west monsoon periods, it forms a felt-like skin which on drying curls up into sheets of considerable tenacity roughly hexagonal in shape and about three sq ft in area During the cold weather period it forms a well-defined skin, not so thick or tenacious as the last-mentioned which, on drying, curls up in sheets of about ¾ square foot in area It possesses some tenacity and is distinctly separate from the sand Immediately after heavy rainfall, i e, in the north-east monsoon period when the water contains comparatively little organic matter, the sedimentary skin is thin, and drying separates into quite small patches which are not readily detached from the surface sand'

There appears to be normally no further growth of algae in the sedimentary skin due to the fact that the sun's rays do not seem to penetrate through 3½ to 4 ft depth of water This is confirmed by the fact that the depth of visibility using Secchi's disc does not exceed 100 cms or 3¼ feet in raw water

(iv) *Gelatinous Layer*

The lower layer below the sedimentary skin is the gelatinous layer which corresponds to the bottom layer described above wherein 'peptonisation and hydrolysis of the albuminoids take place by means of the organisms growing and retained in the filtering skin' This gelatinous layer in the Madras sand filters is well marked for a depth of 1 5 inches below the surface of the sand and sometimes can be seen by the eye to extend to a depth of 9 inches or so. The sand grains in this layer are surrounded by a jelly-like substance which gives the sand a certain tenacity so that it can be kneaded with the fingers as if it were mixed with clay

It has been found in actual practice that on removal of the dense sedimentary skin, the filter continued to work for a considerable period This removal of sedimentary skin has been repeated with advantage several times before removing and washing the gelatinous layer, whenever filters were not sufficient to cope with the city's requirement The absence of a sedimentary skin contributed perhaps very largely to the deterioration in the bacterial efficiency. Usually 1-2 inches of this sand layer was removed every time for washing and cleaning.

(v) *Black Sand Layer.*

A black layer about which no mention has been made so far in any literature on sand filters was always found to commence just below the two layers described above and to extend from two inches to the entire depth of the fine sand layer The longer the life of the filter the greater was the depth of this black layer

This black sand has been examined by Dr Simonson (*vide* p 60, Report of the Committee appointed in G O No 1576 M, 15th September, 1917) who found that '(i) Nitrogen is absent from all the specimens Kjeldahl determination, (ii) the black specimens contain a relatively considerable quantity of sulphide, (iii) there is only the merest trace of sulphate present in the sand from the centre of the beds and no sulphide, and (iv) the black specimens contain sulphate especially after exposure to sunlight and air' Further, that 'From these experiments it would appear that lack of aeration is the cause of black colour and it (black colour) would disappear if there were no dead ends' Iron sulphide according to him 'may be due to the following series of changes —sulphur (from albumen)—iron sulphide—iron sulphate (due to air oxidation) and this passes away dissolved in the water'

Dey and myself (1934) have given a different explanation for the occurrence of the black sand layer based on a detailed study of the conditions It is reproduced below 'The depth of fine sand in the Madras sand filters varies from 9 to 24 inches About 0 5% of iron is present in the sand When a slow sand filter goes out of action it is found that. (1) the entire sand from the coarse sand layer, and gradually extending upwards till the filtering skin or 'schlammdecke' is reached, is black (due to FeS), depends upon the life of a sand filter—the longer the life the greater the formation of black sand, (2) the top portion of fine sand (about 6") contains more iron (0 60%) after each run of a sand filter, although washed sand is used every time that a filter is started, (3) sand, after turning black due to FeS in a filter bed, contains more sulphur than the sand which was not used in a sand filter Therefore it appears from (2) and (3) that sand as it is used in the filters gathers to itself more and more of iron and sulphur and the process of such accretion is easily explained'

Table showing the results of analyses of different specimens of sand

Description of sand.	Fe_2O_3	CaO	MgO	SO_3
1 Fresh unused river sand	0·49	0 026	0 035	.
2 Used but washed sand from Bed No I	0 48	0·024	0·036	0 010
3 Top portion (6") of sand from Bed No I after a run	0 57	0 020	0·032	0·014
4. Bottom portion of black sand from Bed No. I	0·46	0·028	0·035	0·020

'The lake soil being laterite, and hence rich in iron, the latter usually in the form of brownish ferric hydroxide, is slowly deposited on the top 6" of the fine sand layer, especially during the summer months.'

'The H_2S produced by sulphate reduction is fixed chiefly as the sulphides of calcium, magnesium and iron in sand The black iron sulphide when exposed to the sun for purposes of cleaning is converted, at least, practically, into sulphate (Van Hise) There is a tendency for the iron content in sand to go on increasing There is no reason to suppose, making an allowance for the passage of soluble iron compound, that at any time is the iron content likely to decrease The water, besides carrying iron, contains soluble sulphates and negligible sulphur bearing proteins The sulphates are reduced by the action of sulphate-reducing bacteria for which the presence of organic matter is also necessary The sulphate of iron yields FeS, which yields up its S content in the form of H_2S, that either escapes or again acts on the fresh supply of iron in the water to form black iron sulphide How exactly this reduction of sulphates to sulphides takes place has been explained already under chemical conditions' (pp 252–263)

In this connection a brief review of the results obtained by Ellis (1925) in his investigation into the cause of the blackening of the sand in parts of the Clyde Estuary will be extremely interesting He first examined bacteriologically whether the blackness was due to any sewage pollution He found (i) no *B Coli communis* in almost all the samples he examined while he found the total number of bacteria to range from 10,000 to 3,000,000 per gram of sand 'The large number obtained for the total count indicated an enormous amount, relatively, of organic matter large enough to be able to support a very large number of organisms which are absolutely dependent upon organic matter for their sustenance And yet the organic matter harboured no representative of *B. Coli*, a fact which indicates clearly that sewage pollution was not the cause of the presence of this organic matter'

'What is of much greater interest to us in this study is (ii) that the black colour disappeared on free exposure to the air, and this fact precluded, of course, an organic origin to the black material'

(iii) A chemical analysis showed that the black sand consisted of 0·36 to 0·53% of total iron and of 1·2 to 3 0% of organic matter, and to be ferrous sulphide (iv) He found that the predominating bacteria in the black sand was one bacillus, of 1μ in thickness and of a variable length but averaging four to six times the thickness By making cultures of the organism on agar slopes, suspending a strip of filter paper, dipped in lead acetate over the surface of the culture, it was easy to demonstrate the fact that sulphuretted hydrogen was evolved from the cultures whilst the individuals were in process of growth and multiplication. (v) From a study of the geological character of the drainage area he found that it consisted almost entirely of basaltic lavas rich in iron (10 to 15%); and therefore it was not surprising that there should be a fair quantity of iron in the composition of the sands on the shores of the

Clyde. (vi) From a knowledge of the physiology of iron bacteria he concludes that under certain circumstances, in certain waters iron is found in solution combined with some organic radicle 'Further, the iron bacteria thrive best in nature, in water which has passed over boggy country or open moorlands This water picks up in solution organic matter that is liberated as a result of the decomposition of plants The decomposition of ferric hydroxide on the membranes of the iron bacteria shows that such water may also contain iron in solution' From these facts he concludes that 'ferrous sulphide is the compound responsible for the colouring of the sand' He explains 'We know from our researches on the iron bacteria that water containing this kind of organic matter is capable of taking up iron in solution It is probable, therefore, that much of the iron is carried away in solution, in combination with organic matter Then, when the water with the iron in solution laps the shores of the Clyde, the organic matter is taken out of it by the activity of the bacteria, and the iron combines with the hydrogen sulphide liberated by the same organisms When iron combined with organic matter is under other circumstances metabolically treated by the iron bacteria, the iron is separated from the organic matter, but as there is no reducing agent present like hydrogen sulphide the iron instead is oxidised to ferric hydroxide'.

Points raised by Simonson and Ellis examined with reference to the formation of FeS in the Madras Slow Sand Filters

A different explanation is given for the formation of FeS at Madras by the author

(*a*) The blackening of sand is due to FeS, (*b*) there is no sewage contamination, for *B Coli* has been found to be in ±60 c c in the majority of samples and also because the total colonies count does not exceed 500 per c c on nutrient agar at 37°C after 48 hours, (*c*) the oxidation of ferrous sulphide into sulphate takes place on exposure to air, and (*d*) that iron bacteria play an important rôle in its formation.

The author does not agree with Simonson when he says that S for FeS is derived chiefly from albuminous substances deposited on the surface of the sand filter The proportion of organic sulphur to inorganic sulphur in one litre of Red Hills Lake water has been estimated and it has been stated that organic sulphur is practically negligible while inorganic S calculated as SO_3 varied from 20·3 to 24 0 mg per litre (Dey and Ganapati, *l c*). In support of this view, I have also cited Peterson, Fred and Domogalla (1925) who found that cystine, the sulphur containing amino-acid, varied from 1·5 to 7·5 mg. per cubic meter in the different lakes studied by them. So it follows that practically the only source of sulphur for FeS is the inorganic sulphate of raw water.

Then, the presence of the sulphate reducing organism Beijerinck's *Spirillum desulphuricans* in the lake water and in the sand filters has also been shown by me (Dey and Ganapati, *loc cit*) Bunker (1936) has also stated that in nature and industry these sulphate reducing bacteria are shown to be responsible for blackening of mud, and for the deposition of metallic sulphides In the case of the Clyde Estuary it is quite probable that the salt water *Spirillum*, *Microspira aesturii* of Van Delden (*l c*), is the more important organism responsible for the formation of FeS than the bacillus isolated by Ellis, who had probably not thought of sulphate reduction as a possible way for the formation of FeS

(vi) *Nitrification in the Slow Sand Filters*

Nitrifying bacteria have been reported to flourish on the ammonia, nitrites and soluble organic products (Rideal and Rideal, *l c* , Raju, *l c*) emanating from the filtering skin in all sand filters of Europe The experience at Madras is quite the reverse Though ammonia, in fairly large amounts, has been found to be present in the effluents from the Madras slow sand filters, nitrites or nitrates have not been detected at any time This shows that either nitrifying bacteria are absent or if they are present conditions are inimical

Fowler (1935) considers that certain conditions are necessary for nitrification They are not found in the Madras slow sand filters For nitrification the favourable conditions are Presence of oxygen and of a base and some phosphates are essential The presence of excessive amounts of ammonia or of organic matter are prejudicial (Winogrosky) Conditions unfavourable in every way have been found in the Madras slow sand filters (*vide* Chemical Conditions) So nitrification does not take place in them

(vii) *Microflora in the Filtrate of Madras Slow Sand Filters*

(*a*) *Diatoms and Iron bacteria* —When a slow sand filter is started for the first time its run can be divided into two periods (*a*) the period during which H_2S is absent, and (*b*) the rest of the run when H_2S is present The microflora is entirely different in each period In the first period when the production of sulphuretted hydrogen does not take place for a week or two, the filtered water chambers and weirs are coated with a yellowish brown growth which gradually turns dark brown This consists of several species of diatoms *Synedra ulna*, *Synedra ulna* var *impressa*, *Cymbella affinis* and *Navicula* sp. and an iron bacterium *Leptothrix ochraceae* The brown colour is due to hydrated ferric hydroxide present in its sheath

(*b*) *Sulphur bacteria* —Later, when H_2S begins to appear, the brown growth is interspersed with colourless gelatinous growths, on the weirs and walls of the filtered water chamber, and about a week later still, when the gas is present in appreciable quantities, the walls of the chamber are covered to a depth of about one foot from the surface in the Corporation filters, while in the case of the small Govt experimental filter the entire regulating outlet was filled with the colourless growth in long trailing filaments. This is identified to be a mixture of *Beggiatoa minima, Sphaerotilus natans, Thiothrix nivea* and a new sulphur bacterium (?) The colourless growth is seen in some cases in the form of petals arranged one above the other as in the case of a lily flower When the gas production is at its maximum, *i e*, towards the end of a run during March to September, globular, colourless gelatinous growths are seen floating in the filtered water chamber and often sticking to the sides. Jackson (1901-1902) has stated that towards the end of the 19th century iron bacteria in water supplies had caused serious trouble in numerous cities in both America and Europe

Reference to literature regarding the presence of *Leptothrix* in nature goes to show that it is generally present in the iron-bearing surface waters of bogs, streams and springs Harder (1919) has found it in mine waters in the iron range of central Minnesota, in the lead and zinc regions of South Western Wisconsin and in chalybeate springs on a small creek west of Lake Kegona, Molish (1926) has seen it in the rice fields of Japan, Ellis (1925) in several parts of England, Choloday (1926) in Russia, Hirst (1920) in Colombo Water Works Biswas (1930) reports its presence in the filtered water of the Calcutta Water Works

Harder (*l c*) has stated the conditions necessary for the growth of *Leptothrix ochracea* They live on the surface of underground waters, the temperature within moderate limits has no effect on them The quantity of iron required is small and it is found in water with 5 2 p.p m of Fe_2O_3 The amount of organic matter in solution is a limiting factor to a certain extent.

All the varieties of bacteria isolated in the case of Red Hills Lake water (*vide* Chapter I) have been isolated from the filtrates from the Madras slow sand filters So, the presence of iron bacteria in the filtrates from slow sand filters would show that these bacteria are active inside the filtering media and that they precipitate iron hydroxide in the early stages which are turned into soluble ferrous carbonate by carbonic acid (Waksmann, 1936) Thus the presence of more iron in the filtered water than in R W is easily explained (*vide* Chemical Conditions) This is confirmed by another observation also Sulphur bacteria towards the end of the run turn black, and the black colour is discharged by the addition of dilute HCl Iron in the filtrate in the form of ferrous carbonate reacts with H_2S forming black iron sulphide, and the black colour is discharged by the addition of dilute HCl. The sulphur bacteria which was originally colourless and later acquired a black colour again becomes colourless.

Colourless Sulphur bacteria —The second stage in the microbiology of the Madras slow sand filters is the formation of the colourless sulphur bacteria Their appearance synchronises with the production of H_2S in the effluents. But they are not responsible for the formation of hydrogen sulphide (Lafar, *l c.*).

The standard conditions under which the colourless sulphur bacteria appear in nature are given in Bavendamm's monograph (*l c*) on 'Colourless and Red sulphur bacteria' Their appearance is dependent upon five conditions, which are satisfied in the Madras slow sand filters also (i) Hydrogen sulphide helps the growth of sulphur bacteria, for without it there is no life and motion for them In the Madras filters the gas is produced in appreciable quantities so that the growth of the bacteria is encouraged in the filtered water chambers and other places in the Water Works system (ii) The movement of the water in which they occur exerts some influence, for they are not to be found in quickly moving waters Madras filters working at four or six inches vertical per hour offer suitable conditions for their growth (iii) The influence of oxygen is also noticeable inasmuch as the organisms cannot live without it They are therefore seen growing in long trailing filaments on the walls of the filtered water chamber near the surface, on filter weirs and underground reservoirs (provided with ventilators) where they get oxygen from the air and the sulphuretted hydrogen from the filtrates They are not found in the central collecting drains of filters, where oxygen is practically absent (iv) Warmth favours sulphate reduction and the development of saprophytic bacteria so that in summer the output of sulphuretted hydrogen is very large and consequently this season is best suited for the growth of the organisms under discussion In Madras they have been found growing in abundance in the hot weather and south-west monsoon periods. (v) The water must be alkaline to neutralise the sulphuric acid formed as a result of oxidation of hydrogen sulphide by these organisms The pH of raw water is 8 5 and of filtered water about 7 2 showing that the filtered water is evidently favourable for their growth

Slime formation by sulphur bacteria

Ellis (1932) has stated that slime formation is an important characteristic of the sulphur bacteria and that *Beggiatoa alba* forms a considerable amount of slime under certain unfavourable conditions and that in the case of *Thiothrix* the slime formation is normal The formation of globular colourless gelatinous growths towards the end of a filter run is probably an instance of slime formation by the sulphur bacteria present in the filtered water chambers. The findings of Ellis and others are confirmed as regards the slime forming tendency of colourless sulphur bacteria—*Beggiatoa* and *Thiothrix*—found in the Madras sand filters.

Attempts were made as early as 1915 to get rid of the sulphur bacteria, which was then described as 'whitish gelatinous stuff' by chemical treatment One such attempt was made by Madeley (1918) by 'emptying the filters and passing permanganate solution up the outlet drain and into the underground drainage system. This treatment was continued whenever a filter was out of use for cleaning. This was discontinued after 1915 as the cost of permanganate rose considerably'. It was claimed that this measure brought the growth within manageable proportions, but it still appeared in some filter outlets than in others

The object of applying permanganate solution into the underground drainage system was probably to kill the white growth which the authorities of the day then thought was growing in abundance there Later investigations by the author showed that the 'white growth' was never seen inside the underground drainage system of a slow sand filter, and this observation is in accordance with the physiology of colourless sulphur bacteria

Significance of sulphur granules seen outside the cells of colourless sulphur bacteria

It has been shown while discussing the physiology of the colourless sulphur bacteria that H_2S is oxidised by them into water and sulphur according to the equation

$$H_2S + O \longrightarrow H_2O + S$$

and that the sulphur thus liberated is stored inside the cells of these bacteria. Also it has been stated that in the absence of H_2S the sulphur stored inside their cells is used up for its metabolic processes It is also known that in the slow sand filters H_2S is always present If such be the case, how are we to account for the formation of sulphur granules seen outside the cells of the sulphur bacteria gathered from the Madras slow sand filters

This can be accounted for in two ways Either a chemical or a biological or both processes must be taking place It is quite likely that the amount of H_2S not used by the sulphur bacteria are oxidised in the presence of oxygen into water and sulphur, thus resulting in the formation of sulphur granules outside the cells of these bacteria

It is known also that the group of bacteria known as the thionic acid bacteria (Ellis, 1932, Waksmann, 1931) are able to oxidise sulphur compounds like the sulphur bacteria but the former differ from the latter in that they do not store sulphur in their cells It is quite probable that one of this group identified by Nathanson (cited by Ellis, 1932) and later isolated by Beijerinck (cited by Ellis, *l.c*) is responsible for the occurrence of sulphur outside the cells of the sulphur bacteria Sterilised Beijerinck's medium (*vide* Ellis, 1932, p 221) when inoculated with a small quantity of the colourless sulphur bacteria was covered with a film of sulphur in which were numerous bacteria consisting of small thin rods, very motile and non-sporing The control flask showed no change Further tests are being made to confirm this Or it may be a case similar to what has been noticed by Van Niel (*l c*) during the study of the flora occurring in and around the hot springs of Yellow-Stone National Park where 'white flocks were frequently observed which macroscopically showed the greatest possible resemblance to *Thiothrix* Microscopical observations showed, however, that although the flocks contained large amounts of sulphur, this was not present in the cells, but was partly attached to the outside and partly loose The organism consisted of colourless filaments which could very well have been *Thiothrix* filaments but for the much smaller width of the cells (below 1μ) These examples tend to show, therefore, that there exists a number of organisms which are quite closely related to the typical, sulphur storing bacteria but differ from these by the fact that the sulphur is not stored inside the cells The resemblance to the 'sulphur bacteria' concerns the shape of the cells only The size is always smaller, however So, a further detailed study alone can show which of these agencies are responsible for the presence of sulphur granules seen outside the cells and lying loose in the filtered water chambers of the Madras sand filters Which of these processes are taking place is being worked out and will soon be published as a separate communication The results obtained so far go to show the existence of one of the thionic acid bacteria (Beijerinck, *l c*), but since the organism has not been correctly identified its physiology and morphology is not attempted here just now.

Purple coloured sulphur bacteria

Purple coloured sulphur bacteria have been cultured from the black bottom mud of Red Hills Lake (Chapter II) following the method of Van Niel But it was not found in the filtered water chambers of the Madras slow sand filters at any time during the past 25 years It was thought likely that it might be present if cultivated under suitable conditions The medium of Van Niel was therefore used It was sterilised according to the directions given by him and a small quantity of the colourless sulphur bacteria was added to one of the bottles and was exposed to electric light in a dark room Within a week the bottle was coloured rose red, and later brick red On examination the red coloured organisms consisted of circular balls, in singles, pairs or in groups of 3 or 4, each colony containing only one or two sulphur granules

The organisms resembled those of the thiocystis type shown by Van Niel on p 64 of his paper Further experiments are in progress in the laboratory of the author for studying purple-coloured sulphur bacteria from the Red Hills Lake water.

Physiological groups of Bacteria found in the filtrates from Slow Sand Filters.

(1) Colourless, thread forming sulphur bacteria accumulating S within their cells.

(2) The colourless organisms not forming threads and containing S within their cells, also acting on H_2S.

(3) Colourless bacteria that do not accumulate sulphur within their cells but produce sulphur abundantly from thiosulphate, H_2S, etc , outside their cells.

(4) Purple coloured S bacteria

(5) Purple coloured sulphurless bacteria.

(6) Ammonifying bacteria

(7) H_2S producers from all sulphur compounds excepting sulphates

(8) H_2S producers from sulphates

(9) Iron bacteria—*Leptothrix ochracea*

General Summary

1 Slow sand filters have always been considered to be most satisfactory for treating a water of low turbidity and colour One would have expected the same results from slow sand filters when they are applied to impounded surface waters in the tropics Besides, they should be more popular here in view of the fact that the cost of land in India is cheap, labour is cheap and so a city can afford to have a number of them

2 But wherever they are in use (Salem, Adoni, Madras and Baroda) for purifying impounded surface waters they have not proved successful The trouble is (i) the production of sulphuretted hydrogen in the effluent and (ii) the poor bacteriological quality of the filtrates

3 So far, no one has attempted to make a bio-chemical study of this method (slow sand filtration) excepting the Government Committees who have made a series of small scale experiments with the Red Hills Lake water employing various methods of purification

4 A thorough study of the various bio-chemical changes taking place in the Madras slow sand filters (gathered during the past 25 years) is given here in the form of a monograph

5 The changes taking place inside the Madras slow sand filters can be compared to the bottom of tropical lakes where organic and inorganic sediments accumulate Ruttner (1931) has shown that in the bottom of deep tropical lakes decomposition of organic matter takes place at a much greater speed at a temperature of about 25–30°C according to Vant Hoff's R G T rule So there is the formation of large amounts of free CO_2, free ammonia, sulphuretted hydrogen, and also consumption of dissolved oxygen, etc , takes place In the same way in the case of a Madras slow sand filter, the prevailing temperature of about 30° appears to be responsible for all the ills found in them At that temperature there is an increase of free ammonia, carbonic acid, sulphuretted hydrogen, etc., and disappearance of dissolved oxygen due to increased bacterial activity inside the filters. Sulphuretted hydrogen is due to reduction of sulphates at the optimum temperature of about 30°C. by the strictly anaerobic *Spirillum desulfuricans* Sulphur bacteria (colourless) have been seen in the filtrates during the period of H_2S production. Before the production of H_2S iron bacteria are seen.

6 All the attendant biological phenomena noticed in the slow sand filters have been traced at the lake, the source of the city's water supply

7. It is therefore concluded that the method of slow sand filtration is not suitable to purify impounded surface waters of the type of Red Hills Lake Rapid filtration appears to be the most suitable method of purification for tropical impounded surface waters.

The author in conclusion wishes to thank Rao Bahadur Dr C S Govinda Pillai and Dr P Sadasivan for their permission to publish the paper and to Prof Dr M O P Iyengar for help in the identification of phyto-plankton, and to Prof Dr P A Chaippuis for the identification of zoo-plankton and to Dr Gilbert Fowler for his valuable suggestions relating to its publication

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TABLE I

Lake Level and some of the Important Chemical Results for Raw Water (averages of weekly determinations for 12 months) with their correlation coefficients (Pearson's)

Month.	Average lake level in feet	Temp °C.	Turbidity.	Alkalinity	Dissolved oxygen c c /L	Albuminoid N	Oxygen absorbed	Chlorine	Sulphates SO_3
	A	B	C	D	E	F	G	H	I
March, 1929	62·63	28·13	12·0	10·30	4 57	0 038	0 154	4 79	1 81
April	61 66	30 75	12·0	10·30	3 45	0 042	0 179	5 24	1 97
May	60 55	30 13	12·0	10 75	3·45	0·050	0 187	5 50	2 06
June	58·18	31 38	14 0	10 78	3 18	0 055	0 191	5 68	2 12
July	57 92	31 38	15 25	10 56	3 23	0 049	0 221	5 86	2 19
August	56 87	28 88	15·0	11 30	3 54	0·053	0 224	6 03	2 25
September	55 82	28 75	14 75	11 22	3 54	0·056	0 217	6 40	2 40
October	55 78	29 50	16·50	11 18	3 46	0 049	0 201	6 30	2 35
November	61 98	27 75	31 75	8·08	4·09	0·031	0 157	3 90	1 42
December	65·08	26·38	14·50	8 52	4 75	0 032	0 131	3 46	1 26
January, 1930	65 21	27 25	13·00	9 52	5 16	0 045	0 155	3 28	1 19
February	65 47	27 88	12·00	9 72	5 26	0 031	0 175	2 93	1 05

Pearson's correlation co-efficients between

(i)	A and B	—
(ii)	A and C	−0·07
(iii)	A and D	−0 76
(iv)	A and E	+0·97
(v)	A and F	−0 78
(vi)	A and G	−0 86
(vii)	A and H	−0 95
(viii)	A and I	−0 94
(ix)	C and G	−0·01
(x)	E and G	−0 74
(xi)	E and C	−0·07
(xii)	B and E	−0 96
(xiii)	G and I	+0 80

TABLE II

Temperature and Dissolved Gases in the Raw Water and filtrates from different depths of a typical Madras Slow Sand Filter

Date of starting—8-6-34, stopped on 28-6-34.

Date of sampling.	Temperature (°C.)					Dissolved Oxygen (c.c./L.)					Carbon dioxide Mg/L.														
	Raw water	Filtrate.				Raw water	Filtrate.				Raw water			1st tap			2nd tap			3rd tap.			4th tap		
		1st tap.	2nd tap.	3rd tap.	4th tap.		1st tap	2nd tap	3rd tap	4th tap.	Free CO_2	CO_3	HCO_3	Free CO_2	CO_3	HCO_3	Free CO_2	CO_3	HCO_3	Free CO_2	CO_3	HCO_3	Free CO_2	CO_3	HCO_3.
8-6-34	30·5	30·4	30·4	30·6	30·5	4 13	2 86	1 45	0·09	0·12	nil	7 5	108 3	2 2	nil	123 5	3 8	nil	123 5	4 4	nil	125 0	4 4	nil	126·6
11-6-34	30·7	30·2	30·2	30·4	30·3	3·68	1 69	1 51	0·00	0·00	„	12 0	97 6	4 4	„	118·9	4 4	„	122·0	4 4	„	125·0	5·0	„	125·0
16-6-34	31·0	30·8	30·2	30·2	30·0	3 65	1 55	0·06	0·03	0·03	„	7 5	101 3	4 4	„	122·0	6 6	„	129·6	6·6	„	132·7	7 7	„	129·6
18-6-34	31 1	30·6	30·4	31·0	31 3	4 34	0·33	0·03	0·03	0·03	,	12·0	103 7	3 3	,	123 5	4 4	„	123 5	6·6	„	132 7	6·6	„	135·7
27-6-34	29·0	29·2	29·1	29·6	29·6	4 45	0·87	0·03	0·03	0·00	,	13 5	97 6	4 4	„	125 5	5 5	„	131 1	6 6	„	135 7	8 8	„	128·1
							Date of starting—2 7-34					Date of stopping—14-7-34.													
3-7-34	28·8	28·2	28 3	28 4	28 4	4 24	2 46	0 09	0·01	0·01	nil	7 5	111 3	3 3	nil	123 5	4 4	nil	123 5	4 4	nil	126·6	5 5	nil	125·0
6-7-34	28 4	28·2	28 1	28·6	28 4	4·60	0·90	0·31	0·06	0·03	„	12·0	105·2	3 3	„	125 0	4 4	„	128 1	4 4	„	129·6	4 4	„	125·0
10-7-34	28·6	28 2	27 8	28 2	28·0	4·95	0·17	0·06	0·03	0·03	„	16·5	93·0	3 3	„	123 5	4 4	„	128 1	5 5	„	134 2	5 5	„	132·7
13-7-34	29·8	29·3	28·8	29·0	29·0	4 77	0·09	0·06	0·06	0·03	„	9·0	105 2	3 3	„	125·0	4 4	„	128 1	4 4	,	134 2	4 4	„	134·2

1st tap located at 1 *foot* below the surface of fine sand.
2nd tap located at 1' 9" below the surface of fine sand.
3rd tap located at 3' 3" below the surface of fine sand (in coarse sand)
4th tap located at 4' 0" below the surface of fine sand (beneath the bricks)

TABLE III.

1st Run—Dissolved Oxygen

Description.	1st day		3rd day		8th day		10th day		19th day		REMARKS.
	D O in c c /L	Diff	D O in c c /L	Diff	D O in c c /L.	Diff	D O in c c /L	Diff	D O in c c /L	Diff	
Raw water	4·13		3·68		3·65		4·34		4·45		
Effluent from 1st tap	2·86	1·27	1·69	1·99	1·55	2·10	0·33	4·01	0·87	3·58	
,, ,, 2nd tap	1·45	1·41	1·51	0·18	0·06	1·49	0·03	0·30	0·03	0·84	
,, ,, 3rd tap	0·09	1·36	0·0	1·51	0·03	0·03	0·03	0·0	0·03	0·0	
,, ,, 4th tap	0·12	0·03	0·0	0·0	0·03	0·0	0·03	0·0	0·0	0·0	

2nd Run—Dissolved Oxygen

Description	2nd day		4th day		8th day		11th day		REMARKS
	D O in c.c./L	Diff.	D O in c c /L	Diff	D O in c c /L	Diff	D O in c c /L	Diff	
Raw water	4·24		4·60		4·95		4·77		
Effluent from 1st tap	2·46	1·78	0·90	3·70	0·17	4·78	0·09	4·68	
,, ,, 2nd tap	0·09	2·37	0·31	0·59	0·06	0·11	0·06	0·03	
,, ,, 3rd tap	0·01	0·08	0·06	0·25	0·03	0·03	0·06	0·0	
,, ,, 4th tap	0·01	0·0	0·03	0·03	0·03	0·0	0·03	0·0	

1st tap located at a distance of 1 foot from the surface of fine sand
2nd tap located at a distance of 1′ 9″ from the surface of fine sand
3rd tap located at a distance of 3′ 3″ from the surface of fine sand
4th tap located at a distance of 4′ 0″ from the surface of fine sand
The 4th tap represents the final effluent

TABLE III(*a*)

1st Run—Free Carbon dioxide

Description.	1st day.		3rd day		8th day		10th day		19th day.	
	Mg./L.	Diff.	Mg./L	Diff.	Mg /L	Diff	Mg /L	Diff	Mg /L	Diff.
Raw water										
Effluent from 1st tap	2 2		4 4		4 4		3 3		4 4	
" " 2nd tap	3 3	−1·1	4 4	0 0	6 6	−2 2	4 4	−1 1	5 5	−1 1
" " 3rd tap	4 4	−1 1	4 4	0 0	6 6	0 0	6 6	−2 2	6 6	−1 1
" " 4th tap	4·4	0·0	5 0	−0 6	7 7	−1 1	6 6		8 8	−2 2

2nd Run—Free Carbon dioxide

Description.	2nd day.		4th day		8th day		11th day	
	Mg /L	Diff	Mg /L	Diff	Mg /L	Diff	Mg /L	Diff
Raw water								
Effluent from 1st tap	3 3		3 3		3 3		3 3	
" " 2nd tap	4 4	−1 1	4 4	−1 1	4 4	−1 1	4 4	−1 1
" " 3rd tap	4 4	0·0	4 4		5 5	−1 1	4·4	0·0
" " 4th tap	5·5	−1 1	4 4	0·0	5 5	0·0	4 4	0·0

TABLE IV

Showing the Chemical Results of 'The Control Sand Filter' working at 4" vertical per hour

Date of { Starting—28-1-29
Stopping—29-5-29 } Depth of fine sand 36.

Expressed in parts per 100,000

	Raw Water											Filtered Water,												
Date.	Total solids	Total hardness.	Chlorine.	*p*H.	Am N	Alb. N	Abs Oxy	Nitrite	Nitrate	Dis. Oxy c.c. per litre	Temp. °C	Total solids.	Total hardness	Chlorine	*p*H.	Am N	Alb N	Abs Oxy	Nitrite.	Nitrate	Dis. Oxy c.c. per litre.	Temp °C.	Smell of H_2S.	Iron (Ferrous)
6-3-29 .	20·0	5·0	4·62	8·2	·002	·036	142	nil	nil	5·0	28	19 6	5·0	4·62	7·4	·004	·018	116	nil	nil	1 2	26·5	Present	+
10-3-29	21·0	5·0	4·62	8·2	·002	034	154	„	„	5 0	28	20 2	5·0	4·62	7 4	·006	018	128	„	„	1·0	27·0	„	+
14-3-29 .	20·6	5·0	4·62	8·2	·003	·034	150	„	„	5·0	28	19·6	5·0	4 62	7 4	·007	018	152	„	„	1 0	27·0	„	++
18-3-29	21·6	5·0	4·62	8 2	·003	·045	144	„	„	4·6	28	21·0	5·0	4·62	7 4	009	020	160	„	„	1·0	27·0	„	++
22-3-29	21·6	5·0	4·62	8 2	·002	·030	156	„	„	4 3	28	21 0	5 0	4·62	7 4	·010	·020	175	„	„	1·0	27·0	„	++
26-3-29	21 4	5·0	4·62	8 2	·002	·031	162	„	„	4 0	28	21·0	5 0	4·62	7 4	012	018	188	„	„	0·8	27·0	„	++
30-3-29	20·8	5·0	4·62	8 2	·002	·032	164	„	„	3 7	28 5	20·0	5·0	4 62	7 4	·012	·020	196	„	„	1·0	27 0	„	++
3-4-29	21·2	5·0	4·62	8 2	Trace	038	159	„	„	3 7	28 5	20 6	5·0	4 62	7 2	017	020	198	„	„	0 6	27·0	Strong	+++
7-4-29	21 4	5·0	4·97	8 2	002	034	172	„	„	3·7	29·5	21 0	5·0	4 62	7 2	022	·018	196	„	„	0·4	27·0	„	+++
11-4-29	21·6	5·0	4·97	8·2	Trace	·030	160	„	„	3 6	30	21 0	5·0	4 92	7 2	022	018	199	„	„	0 4	28 5	„	+++
15-4-29	21·6	5 5	5 33	8 2	·002	·054	184	„	„	3 4	30	21·0	5 5	5 33	7 2	·025	·020	220	„	„	0·3	28 5	„	+++
18-4-29	21·6	5 5	5 33	8 2	·002	·056	179	„	„	3 3	31·0	21 0	5 5	5 33	7 1	·028	·020	247	„	„	0 2	28 5	„	+++
23-4-29	21 8	5 5	5 33	8 2	·003	·036	172	„	„	3 3	31·0	20 8	5 5	5 33	7 1	·030	·016	264	„	„	nil	28 5	„	+++
27-4-29 .	22·0	5 5	5·33	8 2	·003	040	154	„	„	3 3	31·0	21·0	5 5	5 33	7 1	028	020	262	„	„	„	29·0	„	+++
1-5-29 .	22·4	5·5	5 33	8 2	002	·042	174	„	„	3 4	31 0	21 6	5 5	5 33	7 1	·029	·020	280	„	„	„	29·0	Intense	+++
5-5-29 .	22·2	5 5	5·33	8 2	·002	·038	183	„	„	3 4	31 0	21 4	6·0	5 53	7 1	·028	016	288	„	„	„	29·0	„	++++
9-5-29	22·4	6·0	5·33	8 4	·003	·040	152	„	„	3 6	30 0	21 4	6·0	5 33	7 1	·030	·022	280	„	„	„	29·0	„	++++
13-5-29	22·8	6·0	5·68	8 4	·003	·038	156	„	„	3 6	30·0	21 6	6·0	5·68	7 1	033	018	286	„	„	„	29·0	„	++++
17-5-29	23·0	6·0	5·68	8 4	Trace	·041	184	„	„	3 4	30·0	22 0	6·0	5 68	7 1	·036	·022	298	„	„	„	29·0	„	++++
21-5-29	23·0	6·0	5·68	8 4	„	049	229	„	„	3 4	30·0	22·0	6·0	5 68	7 1	·034	028	298	„	„	„	29·0	„	++++
25-5-29	22·8	6·0	5·68	8 4	·002	·040	165	„	„	3 5	30·0	22·0	6 0	5 68	7 1	038	·030	350	„	„	„	29·0	„	++++
29-5-29	23·0	6·0	5·68	8 4	·003	·042	156	„	„	3 4	30·0	22·0	6·0	5 62	7 1	040	·028	402	„	„	„	29·0	„	++++

N B—(1) H_2S first appeared on 20-2-29, i.e. 23 days after starting the filter

(2) Yellowish brown growth which gradually turned dark brown containing an iron bacteria *Lepthothrix Ochracea* with several species of Diatoms and Infusors was first seen during the H_2S free period.

(3) With the appearance of H_2S in the filtrate, the whole of filtered water chamber was covered with long trailing filaments of colourless sulphur bacteria—*Beggiatoa Minima*, *Thiothrix Nivea*, *Sphaerotilus natans* and another big sulphur bacterium (probably a new species according to H Molisch) besides a considerable number of bacilli, spirilli, cocci, and granules of S outside the cells of the thread bacteria.

TABLE V

1st Run—Bicarbonic Acid (HCO_3)

Description	1st day		3rd day		8th day		10th day		19th day		REMARKS.
	Mg /L	Diff.	Mg /L	Diff.	Mg /L	Diff	Mg /L	Diff	Mg /L	Diff.	
Raw water	108 3		97 6		101 3		103 7		97 6		
Effluent from 1st tap	123 5	−15 2	118 9	−21 3	122 0	−20 7	123 5	−19 8	125 5	−27 9	
,, ,, 2nd tap	123 5	−0 0	122 0	−3 1	129 6	−7 6	123 5	−0 0	131 1	−5 6	
,, ,, 3rd tap	125 0	−1 5	125 0	−3 0	132 7	−3 1	132 7	−9 2	135 7	−4 6	
,, ,, 4th tap	126 0	−1 0	125 0	0 0	129 6	3 1	135 7	−3 0	128 1	7 6	

2nd Run—Bicarbonic Acid (HCO_3)

Description.	2nd day		4th day		8th day		11th day		REMARKS.
	Mg /L	Diff	Mg /L	Diff	Mg /L	Diff	Mg /L	Diff	
Raw water	111 3		105 2		93 0		105 2		
Effluent from 1st tap	123 5	−12 2	125 0	−19·8	123 5	−30·5	125 0	−19 8	
,, ,, 2nd tap	123 5	0·0	128 1	−3 1	129 6	−6 1	125 0	0 0	
,, ,, 3rd tap	123 5	0·0	128 1	0·0	134 2	−4 6	132 7	−7 7	
,, ,, 4th tap	125 0	−1 5	128 1	0·0	134 2	0 0	134 2	−1 5	

TABLE VI.

Showing the relation between Inorganic Sulphate in Raw and Filtered Water and H_2S produced in the Filter Bed No 1 in one run.

Date of starting.	Date of estimation.	SO_3 in Mg per litre			H_2S in Mg per litre		REMARKS
		Raw water	Filtrate	Difference	Calculated from difference of SO_3	Found.	
10th August, 1929 .	14th August, 1929	22·4	20·3	2·1	0·9	0·5	Depth of fine sand 15″
,, .	16th ,, ,,	22·4	20·6	1·8	0·8	1·2	
,, ..	19th ,, ,,	22·5	20·0	2·5	1·1	2·1	Rate of filtration of 6″ vertical per hour
,, .	21st ,, ,,	22·5	19·7	2·8	1·2	3·2	
,,	25th ,, ,,	22·7	20·4	2·3	1·1	4·4	
,, ..	26th ,, ,,						Filter stopped.

TABLE VII

Showing the relation between Inorganic Sulphate in Raw and Filtered Water and H_2S estimated from 10 Filters in the Water Works

Bed No.	Date of starting	Date of examination	Day of run	Rate of filtration in inches	Depth of fine sand in inches	Date of closing	SO_3 in Mg per litre			H_2S in Mg per litre	
							Influent	Effluent	Difference	Calculated from difference of SO_3	Actually found.
1	6th September, 1929	28th September, 1929	22	2″	15″	11th October, 1929	24·0	21·8	2·2	0·9	3·8
2	23rd ,, ,,	,, ,, ,,	5	6″	19″	16th November, 1929	24·0	22·0	2·0	0·8	1·6
3	5th October, 1929	28th October, 1929	23	6″	24″	26th December, 1929	23·4	20·6	2·8	1·3	4·9
4											
5	9th November, 1929	7th December, 1929	28	6″	17″	8th January, 1930	13·2	11·1	2·1	0·9	2·8
6	30th ,, ,,	,, ,, ,,	8	6″	24″	3rd February, 1930	13·2	11·3	1·9	0·8	0·8
7	26th December, 1929	21st January, 1930	26	6″	16″	9th ,, ,,	11·8	9·8	2·0	0·8	1·9
8	20th ,, ,,	,, ,, ,,	32	6″	12″	15th ,, ,,	11·8	10·0	1·8	0·7	1·6
9	3rd January, 1930	14th February, 1930	42	6″	24″	16th ,, ,,	9·2	7·4	1·8	0·7	1·2
10	19th ,, ,,	,, ,, ,,	26	6″	21″	16th March, 1930	9·2	7·6	1·6	0·7	1·0

TABLE VIII

Oxygen absorbed—5′ test—1st Run

Description.	1st day		3rd day		8th day		10th day		19th day	
	Mg./L	Diff	Mg./L	Diff	Mg /L	Diff	Mg /L	Diff	Mg /L	Diff
Raw water					0·043		0·065		0·054	
Effluent from 1st tap			0·024		0·036	+0·007	0·062	+0·003	0·065	−0·011
,, ,, 2nd tap			0·032	−0·008	0·057	−0·021	0·081	−0·019	0·122	−0·057
,, ,, 3rd tap			0·043	−0·011	0·109	−0·052	0·157	−0·076	0·208	−0·086
,, ,, 4th tap			0·070	−0·027	0·154	−0·045	0·183	−0·026	0·180	+0·028

Oxygen absorbed—5′ test—2nd Run

Description.	2nd day.		4th day		8th day		11th day.	
	Mg /L	Diff	Mg /L	Diff	Mg /L	Diff	Mg /L	Diff
Raw water								
Effluent from 1st tap	0·059		0·056		0·050		0·074	
,, ,, 2nd tap	0·069	−0·010	0·056	0·0	0·073	−0·023	0·143	−0·069
,, ,, 3rd tap	0·077	−0·008	0·080	−0·024	0·143	−0·070	0·208	−0·065
,, ,, 4th tap	0·083	−0·006	0·092	−0·012	0·154	−0·011	0·217	−0·009

TABLE IX

Oxygen absorbed—4 hours test—1st Run

Description	1st day		3rd day		8th day		10th day		19th day	
	Mg /L	Diff	Mg /L	Diff	Mg /L	Diff	Mg /L	Diff	Mg /L	Diff
Raw water			0 192		0 143		0 204		0 160	
Effluent from 1st tap			0 160	+0 032	0 099	+0 044	0 187	+0 017	0 156	+0 004
,, ,, 2nd tap			0 184	−0 024	0 131	−0 032	0 190	−0 003	0 174	−0·018
,, ,, 3rd tap			0 184	0 0	0 171	−0 040	0 256	−0 066	0 227	−0 053
,, ,, 4th tap			0 184	0 0	0 197	−0 026	0 281	0 025	0 262	−0 035

Oxygen absorbed—4 hours test—2nd Run

Description	2nd day		4th day		8th day		11th day	
	Mg /L	Diff	Mg /L	Diff	Mg /L	Diff	Mg /L	Diff
Raw water	0 141		0 157		0 179		0 182	
Effluent from 1st tap	0 114	+0·027	0 134	+0 023	0 135	+0·044	0 155	+0 027
,, ,, 2nd tap	0 119	−0 005	0 134	0 0	0 165	−0 030	0 194	−0 039
,, ,, 3rd tap	0 125	−0 006	0 147	−0 013	0 212	−0·047	0 271	−0 077
,, ,, 4th tap	0 129	−0 004	0 155	−0 008	0 221	−0·009	0 297	−0·026

TABLE X

Oxygen absorbed *Monthly averages for Raw Water and Effluent from the Experimental Slow Sand Filter*
(*Averages calculated from G O Nos* 1550, 709 *and* 932)

Year.	January		February		March		April		May		June	
	R.W	S S.F	R W.	S S.F	R W	S S F	R W	S S.F	R W	S S F	R W	S S F
1928 .	0·126	0·079	0 123	0·142	0 135	0 147	0·121	0 272	0·145	0 125	0 131	0 179
1929 .	0·144	0·103	0 131	0 089	0·150	0 136	0 162	0 223	0 160	0 300	0 177	0 233

Year	July		August.		September		October		November		December	
	R.W	S S.F	R W	S.S.F	R W	S S F	R W	S S F	R W	S S F	R W	S S F
1928	0·143	0·293	0·162	0·252	0 190	0 336	0 190	0·193	0·143	0 127	0 136	0 090
1929	0·180	0·219	0·192	0·257	0 207	0 369	0 189	0 284	0 152	0 224		

TABLE XI.

Ammoniacal Nitrogen. Monthly averages for Raw Water and Effluent from the Experimental Slow Sand Filter

(Averages calculated from G O Nos 1550, 709 *and* 932)

Year.	January		February		March.		April		May		June	
	R W	S S.F	R W	S S F	R W	S S F	R W	S S F	R W	S S F	R W	S S F
1928	0·002	0·004	0·003	0·006	0·002	0·012	0·002	0·018	0·002	0·003	0·002	0·005
1929	0·002	0·003	0·002	0·003	0·001	0·005	0·002	0·012	0·002	0·016	0·002	0·015

Year.	July		August		September		October		November		December	
	R.W	S S.F	R W.	S S F	R W	S S F	R W	S S F	R W	S S F	R W	S S F.
1928 ..	0·003	0·016	0·003	0·014	0·002	0·016	0·002	0·013	0·002	0·006	0·002	0·002
1929	0·002	0·013	0·003	0·015	0·003	0·018	0·002	0·020	0·003	0·011		

TABLE XII.

Albuminoid Nitrogen. Monthly averages for Raw Water and Effluent from the Experimental Slow Sand Filter

(*Averages calculated from G O. Nos* 1550, 709, *and* 932)

Year.	January.		February		March.		April.		May		June	
	R.W.	S.S.F.	R.W.	S S.F	R W	S S.F	R W	S S F	R W	S S F	R W	S.S.F
1928 .	0·030	0·014	0·031	0·014	0·037	0·014	0·034	0·015	0·039	0·031	0·039	0·025
1929 .	0·028	0·012	0·032	0·011	0·032	0·014	0·036	0·016	0·036	0·016	0·039	0·022

Year.	July.		August		September		October		November		December.	
	R.W	S.S.F	R W	S S F	R.W	S S F	R W	S S.F	R W	S S F	R W	S S F
1928	0·041	0·025	0·041	0·023	0·043	0·025	0·043	0·029	0·023	0·012	0·020	0·010
1929 .	0·037	0·018	0·044	0·020	0·041	0·025	0·045	0·027	0·033	0·014		

TABLE XIII

Showing the chemical results of 'The Experimental Sand Filter' working at 4" vertical per hour

(Expressed in parts per 100,000)

Started on 1-6-29. **Stopped on 22-6-29.**

Date.	Raw Water									Filtered Water									
	*p*H	Am. N.	Alb. N	Absorbed Oxygen	Nitrite	Nitrate	Free CO_2	Fixed solids	Ignitible matter	*p*H.	Am N	Alb N	Absorbed Oxygen	Nitrite	Nitrate	H_2S	Free CO_2	Fixed solids	Ignitible matter.
5th June, 1929	8 4	002	050	188	nil	nil	Trace	17 8	6 8	7 2	015	020	190	nil	nil	Present	1 0	16 8	4 6
8th „ „	8 4	·004	056	200	„	„	0 1	18 4	6 6	7 2	020	020	256	„	„	„	1 2	17·0	5·4
13th „ „	8 4	·002	060	184	„	„	0 1	18 0	6 4	7 2	024	022	260	„	„	„	1·0	17 0	6·0
15th „ „	8 4	Trace	·063	200	„	„	0 1	19 0	6 6	7 1	025	022	295	„	„	Intense	1 4	17 8	5·0
17th „ „	8 4	004	056	194	„	„	0 1	19·0	7 0	7 1	030	020	284	„	„	„	1 8	17 8	5·2
21st „ „	8 4	·002	·048	187	„	„	Trace	18·0	7 0	7 1	030	020	312	„	„	„	2 0	17 6	4·8

TABLE XIV

Showing some of the Important Chemical and Bacteriological Results of Bed No 1 working at 6" vertical per hour

Chlorinated Raw Water—Expressed in parts per 100,000—Filtered Water

Date.	Am. N.	Alb N.	Abs Oxygen.	Nitrite.	Nitrate	H_2S.	L.F in ? c c and upwards	Total colonies per c c on agar at 37°C	Am N		Alb N	Absorbed oxygen			H_2S Test	Value for H_2S from absorbed oxygen	L F. in ? c c and upwards	Total colonies per c c on agar at 37°C
									With H_2S.	Without H_2S		Total	By H_2S	By organic matter				
								1st Run started on 2-2-1930				*Depth of sand* 15"						
4-2-30				nil	nil	nil	60 c c.	180	Trace			116			nil		10 c c	600
9-2-30	·004	·036	153	,,	,,	,,	60 c c	60	002		020	104						
10-2-30	·004	·042	153	,,	,,	,,	60 c c	150	003		028	082			Trace		10 c c	480
12-2-30	·003	·036	160	,,	,,	,,	60 c c	180	·008	·006	022	106	·036	070		76	20 c c	600
14-2-30	·004	036	173	,,	,,	,,	60 c c	200	·017	010	019	128	049	079	Strong	1 04	20 c c	600
17-2-30	·004	·040	170	,,	,,	,,	60 c.c	300	013	014	025	130	·052	078	,,	1 11	60 c c	440
19-2-30	Trace	·047	166	,,	,,	,,	60 c c	200	·012	010	018	138	048	090	,,	1 02	5 c c	760
21-2-30	·002	·029	154	,,	,,	,,	60 c c	200	020	015	018	154	077	077	,,	1 64	60 c c	400
24-2-30 .	·001	·042	170	,,	,,	,,	60 c c	100	030	·027	028	170	123	047	,,	2 61	60 c c	240
28-2-30	·002	·025	170	,,	,,	,,	60 c c	120	020	018	026	170	093	077	Intense	1 98	10 c c	740
4-3-30	Trace	·036	163	,,	,,	,,	60 c c.	150	026	020	020	167	107	060	,,	2 27	10 c c	840
5-3-30	·003	·034	169	,,	,,	,,	60 c c	100	039	026	018	209	135	074	,,	2 87	20 c c	460
7-3-30 .	Trace	·056	185	,,	,,	,,	60 c c	250	038	028	025	246	172	074	,,	3 66	20 c.c.	700
10-3-30 . .	·002	·049	·207	,,	,,	,,	60 c c.	100	023	016	025	257	179	078	,,	3 82	60 c c	450
								Stopped on 10-3-30										
								2nd Run started on 21-3-30				*Depth of sand* 12"						
24-3-30	Trace	·036	·160	,,	,,	,,	60 c c.	160	Trace		037	172	066	106	Trace	1 40	10 c c	460
26-3-30 .	,,	·054	212	,,	,,	,,	60 c c	140	011	·012	054	165	097	068	,,	2 06	20 c c	600
29-3-30 .	,,	·038	168	,,	,,	,,	60 c c	80	·018	010	·018	206	·072	134	Strong	1 53	10 c.c	460
1-4-30 .	,,	·034	188	,,	,,	,,	60 c c	100	·044	020	027	250	125	125	,,	2 66	5 c.c.	560
								Stopped on 2-4-30										
								3rd Run started on 7-4-30.				*Depth of sand* 10".						
9-4-30 .	·004	·036	186	,,	,,	,,	60 c c	200	027	·020	·022	181	·077	104	Trace	1 63	5 c.c.	760
11-4-30 .	·001	·047	·182	,,	,,	,,	60 c c.	140	·018	012	040	206	145	061	,,	3 68	20 c.c.	400

14-4-30	·004	·050	251	,,	,,	,,	60 c c	90	036	020	045	207	155	074	Intense	2 83	60 c.c	240
23-4-30	·002	·049	152	,,	,,	,,	60 c.c	100	047	038	045	276	166	110	,,	3 53	20 c.c.	400
25-4-30	Trace	·052	193	,,	,,	,	60 c c	140	022	012	036	284	182	102	,,	3 87	60 c.c.	240
								Stopped on 26 4-30										
								4th Run started on 30-4-30 *Depth of sand* 10″										
2-5-30	·003	054	171	,,	,,	,,	60 c c	200	013	003	027	171	·083	088	Trace	1 76	20 c c.	420
5-5-30	Trace	·045	·177	,,	,	,	60 c c	90	031	011	036	221	116	105	,,	2 47	10 c c.	750
9-5-30			141	,,	,,	,,	60 c c	100				235	141	094	,,	3 00	20 c.c.	430
12-5-30			206	,,	,,	,,	60 c c	80				297	171	126	Strong	3 63	20 c c.	600
14-5-30 .	·002	045	213	,,	,,	,,	60 c c	80	027	018	038	280	160	120	,,	3 40	5 c.c.	700
19-5-30 .	Trace	·045	173	,,		,,	60 c c	180	027	016	036	253	160	093	,,	3 40	5 c c.	700
20-5-30 .	·002	·034	·186	,,	,	,,	60 c c	160	030	020	027	280	160	120	,,	3 40	10 c.c	860
21-5-30	·002	·054	·187	,,	,,	,,	60 c c	100	018	020	027	280	160	120	,,	3 40	10 c c	800
23-5-30	·002	·038	·160	,,	,,	,,	60 c c	200	·045	030	029	267	160	120	,,		1 c c	800
26-5-30 .	Trace	042	150	,,	,,	,,	60 c c	160	029	022	025	312	188	124	,,	4·00	20 c.c.	480

TABLE XV.

Showing the amount of Inorganic and Organic Sulphur in Raw Water

(Calculated as SO_3)

Date of Estimation	SO_3 in Mg per litre			REMARKS
	Sulphur (total)	Inorganic sulphur	Organic sulphur by difference	
7th June, 1929	20 9	20 8	0 1	
28th ,, ,,	21 9	21 8	0 1	
14th July, 1929	22 3	22 2	0 1	
14th August, 1929	22 4	22 4	nil	
7th September, 1929	24 0	23 9	0 1	

TABLE XVI.

Showing the amount of Sulphate and Iron in different specimens of Sand

(Averages of three analyses)

Description of Sand.	Per cent		REMARKS
	Sulphate calculated as SO_3	Iron calculated as Fe_2O_3	
1. Fresh unused river sand		0 047	
2. Used but washed sand from Bed No I	0 018	0 48	
3. Top portion (3″) of sand taken immediately after stopping the Filter No I	0 018	0 57	This sand was not black
4. Bottom portion of black sand taken immediately after stopping the Filter No I and air dried	0 039	0 46	

Symposium on Coal in India.

Under the auspices of the National Institute of Sciences of India, a symposium on Coal in India was held in the rooms of the Royal Asiatic Society of Bengal on the 25th and 26th August, 1939, under the presidency of Brevet-Colonel R N Chopra, C I E, M D, Sc D, I M S It was organised by Dr Cyril S Fox, Director of the Geological Survey of India, and embraced all significant aspects of the important problem of the main fuel resources of India arranged under forty-one subjects as follows —

1 History of the Development of the Coal Industry
2 History of Coal Mining in India
3. The Geology of Indian Coal
4 Reserves of Coal in India
5 India's position in the world as a Coal Producer
6 Fuel Survey of the Coal Seams
7 The Conservation of Coal
8 The present status of the Coal Industry
9 Coal in relation to Metalliferous Industries
10 Coal and the Railways
11 Coal in relation to Power
12 Coal in the Chemical Industry
13 Carbonisation of Coal
14 Liquid Fuels from Coal
15 Briquetting of Coal
16 Gaseous Fuels from Coal (including underground gasification)
17 Domestic Coke
18 Fuel Research
19 Safety in Mines Research
20 Safety in Coal Mining
21 Coal Mines Regulations and Administration
22 Mine Plans and their Value
23 Packing with incombustible material in Coal Mines
24 Fires and Ignition in Coal Mines
25 Fire-fighting and Rescue in Coal Mines
26 Storage of Coal
27 Competitive Conditions in the Coal Trade
28 Indian Export Trade in Coal (Coal Grading Board)
29 Marketing of Coal.
30. Physical characters and chemical constitution of Coal.
31 Methods of Analysis of Coal
32 Coal Cleaning and Beneficiation

33. Sulphur in Coal
34. Moisture in Coal
35 Ash in Coal
36 Volatile Matter in Coal—its nature and properties
37 Classification of Coal—its relation to utilization
38 Petrology of Coal
39 X-ray Analysis of Coal.
40 Botany of Coal Seams
41 State control, rationalisation and nationalisation of the Coal Industry.

Opening Address by Dr. Cyril S Fox

If we may judge from the interesting remarks in the 'Abstracts of Papers', which are to be dealt with in this symposium on 'Coal in India', we are justified in believing that the Council of the National Institute of Sciences of India will have cause for congratulation at the end of the meeting On the one hand they have secured valuable contributions from people who are reliable authorities on the subjects with which they have dealt, and on the other hand contact has been established with many experts in the coal industry of India who probably still do not know what the National Institute of Sciences of India is

Without going too deeply into details I would say that, even before 1902, when the Government of India instituted a Board of Scientific Advice for co-ordinating the work of official scientific departments in this country, to after 1930, when the Government of India was constrained to become a member of the International Research Council, scientists have felt the need of a co-ordinating non-official body which was entirely free of any political element After considerable effort and with the co-operation of the majority of scientists in India, the National Institute of Sciences of India was founded in 1935 in Calcutta

It is necessary to explain that the International Research Council, already mentioned, was the name adopted by a select committee, formed in 1918-19, which had its headquarters in Brussels and representatives in Europe and America The purpose it had was to co-ordinate the work of scientists in all countries throughout the world by means of members on its Council from all countries and representatives of co-ordinating National Research Councils in those countries There was no such representative body in India and the National Institute of Sciences of India was formed with a view to going some way towards creating such an organisation.

The aim of the National Institute of Sciences of India is not merely for the co-ordination of the labours of men of science It has a larger scope. I will quote in order the first three of the eight objectives which this Institute has in view —

(a) The promotion of natural knowledge in India including its practical application to problems of national welfare

(b) To effect co-ordination between scientific academies, societies, institutions, and Government scientific departments and services

(c) To act as a body of scientists of eminence for the promotion and safeguarding of the interests of scientists in India, and to represent internationally the scientific work of India

The preparation of a symposium on 'Coal in India' was undertaken by the Council of the National Institute of Sciences of India under the terms of its first fundamental objective I was not present at that council meeting and so can claim no credit for the selection of 'Coal in India' as the subject of a symposium, but there is no question that this is the most important mineral substance in this country and that coal is still *par excellence* the most valuable mineral fuel in any country The coal production of India in 1938 was over 28 342 million tons valued at rupees 1,064 lakhs

I will now briefly discuss the scope of the symposium on 'Coal in India'. You will see from the arrangement of the papers that the order of treatment is from the history of the coal industry, and coal mining in India specially, to geology and geological considerations with regard to coal reserves, and so to the utilization of coal in India Next, attention is given to questions of coal carbonisation and fuel research generally This is followed by papers on safety in mines, which end with the subject of rescue work in coal mines We then turn to the important question of marketing Indian coal and the details involved in it—cleaning, grading, methods of analysis—and end with remarks on the problem of nationalisation of the coal industry

Before the first paper is now called for reading, I would like to say that although the excellent response to my appeal for papers is evident in the 'Abstracts of Papers', this is not all the assistance and interest that has been shown in our efforts. The leading Calcutta firms who operate collieries in the Damodar Valley have provided the funds and will be our hosts today at lunch at Firpo's Peliti's branch, and at tea here in the Royal Asiatic Society of Bengal I take this opportunity of saying how much we appreciate their kind hospitality

HISTORY OF THE DEVELOPMENT OF THE COAL INDUSTRY

By E R Gee, *M A* (*Cantab*), *F G S*, *Geological Survey of India*

To attempt to deal with this vast subject in any degree of detail in the short space available here is, of course, impossible I therefore propose merely to touch lightly on the early rise of the coal industry, noting briefly the principal landmarks of that period of its history and so pass on rapidly to the events of the present century which have such an important bearing on the state of the industry as it exists at the present day.

As a preliminary, it is perhaps as well to get some idea of the output and uses of coal in various countries at the present time At present, some 50 countries are engaged in the mining of coal (including anthracite, bituminous, lignite and brown coal) and in 1936 these countries produced about 1,280 million metric tons of coal units (lignite and brown coals being converted into coal units thermally equivalent to the average of anthracite and bituminous)

Of this world total, about four-fifths is consumed as fuel and the remaining one-fifth as raw material

As fuel	*Per cent*
Industry (mainly for steam-raising)	30
Railways	15
Electric generating stations	8
Ships' bunkers	2
Collieries	5
For domestic purposes	20
Total	80
As raw material	
Metallurgical works (mainly iron and steel)	15
Gas works	5
Total	20

This world total consisted of:—

Bituminous coal	about	87·7
Anthracite	,,	7·6
Lignite	,,	4·8

The world output of nearly 1,300 million tons was distributed among the various countries as follows:—

[Published August 9th, 1940.

TABLE 1.—Percentages of world output of raw coal by countries, 1934–1936

(*Lignite converted into equivalent coal units.*)

Country	1934	1935	1936.	Cumulative percentage, 1936
United States	32·9	32·3	34·4	34·4
Great Britain	19·6	19·1	18·1	52·5
Germany	13·6	14·9 (*d*)	15·2 (*d*)	67·7
Saar	1·0	(0·9)	(0·9)	
U.S.S.R.	7·5	8·4	8·7	76·4
France	4·2	3·9	3·6	80·0
Japan (*a*)	3·1	3·2	3·0 (*e*)	83·0
Poland	2·6	2·4	2·3	85·3
Belgium	2·3	2·2	2·2	87·5
India (*b*)	2·0	2·0	1·8	89·3
Czechoslovakia	1·7	1·7	1·7	91·0
China (excluding Manchuria)	1·8	1·8	1·6	92·6
Manchuria	1·0	1·0	0·9	93·5
South Africa	1·1	1·2	1·2	94·7
Netherlands	1·1	1·1	1·0	95·7
Australia	0·9	1·0	0·9	96·6
Canada	0·9	0·9	0·9	97·5
Other countries (*c*)	2·6	2·9	2·5	100·0
TOTAL	100·0	100·0	100·0	
Total production (million metric tons)	1144·6	1179·9	1280·4	

(*a*) Without colonies.

(*b*) Including Native States.

(*c*) Of the other countries, the most important are Spain, Hungary, Turkey, Austria and French Indo-China.

(*d*) Including the Saar.

(*e*) Based on final estimate (38·1 million tons) instead of provisional (41·0).

These figures reveal the fact that over three-quarters of the output in 1936 was produced by four countries, the U.S.A. with 34 per cent, Great Britain with 18 per cent, Germany with 15 per cent, and the U.S.S.R. with 8·7 per cent, whilst other countries in Europe accounted for a further 10·8 per cent, giving a total for western Europe and the U.S.S.R. of some 53 per cent of the world's output.

Having got a slight idea of the magnitude and geographical distribution of the coal industry we will now trace briefly the various sequence of events that have had an important influence on its expansion and development.

The early history of the use of these fossil fuels as distinct from that of wood charcoal is somewhat obscure. This lack of reference to the value of coal in early literature merely lends emphasis to the fact that the development of the industry on an appreciable scale is of relatively recent date, being closely bound up with the deforestation of large areas of the countryside, resulting in a shortage of the more obvious and easily won sources of domestic fuel on the one hand and by the wave of engineering invention and attendant rapid industrialisation dating from the latter part of the 18th century on the other

Perhaps the earliest reference in which a definite distinction is drawn between fossil coals and wood charcoal is in the Greek writings of Theophrastus, a pupil of Aristotle who, about the year 371 B C in his treatise 'On Stones', mentions 'fossil substances that are called coals, which kindle and burn like wood coals' occurring 'in Liguria and in Elis, on the way to Olympias,—they are used by the smiths'

In Great Britain, it is most probable that the use of 'stone coal' was known to the Romans at the time of their occupation, for among the ruins of Roman towns, forts, etc especially in Northumberland, coal cinders have been found

Time does not permit me to discuss the etymology of the word 'coal' and I would refer those interested to Dr Fox's memoir entitled 'The Natural History of Indian Coal' But it is apparent, from the nomenclature used in various countries, that fossil coal had been recognised from ancient times in many European countries, and although in India, there appears no definite mention of it in the literature till as late as 1774, it had doubtless been recognised at a much earlier date.

There is evidence to show that coal was mined in Great Britain during the ninth century and certainly in the continent of Europe during the tenth century

Subsequent to that date, the coal industry in Europe expanded appreciably and in Britain, by Tudor times, an important trade had developed between Northumberland and Durham mines and the city of London and coal was exported to northern France In Scotland it was mined for use in local industries

As far back as those early times, the smoke nuisance was realised for it was reported in 1578 that the burning of coal was prohibited in the vicinity of the Palace of Westminster when Queen Elizabeth was in residence To combat this smoke nuisance on the Continent, powdered coal was mixed with loam and made into balls, the resulting fuel proving economical, smouldering gradually away and producing no flame and little smoke This practice continued in Belgium until recent years

By the 17th century, coal was well known throughout Britain and a large part of Europe, and the industry was an extremely profitable one for the fortunate proprietors and land-owners, contrasting with the lot of the miners who worked under the most wretched conditions.

Expansion was assisted by the construction of canals in the European coal-producing countries, giving cheap transport to the sea and to various inland towns.

But by far the greatest impetus given to the coal industry was the invention and improvement of the steam-engine by James Watt of Greenock during the latter half of the 18th century, and secondly, by the introduction of railways, which commenced with the improved locomotives of George Stephenson in 1815

Ease of steam transport both by sea and land not only directly effected a tremendous increase in the demand for coal, but quite naturally gave an enormous impetus to the iron and steel and attendant carbonisation industries, and to manufacturing trades and domestic consumption in general In fact, almost every important engineering invention, so numerous from the latter part of the 18th century onwards, added directly or indirectly to the demand for coal

Blast furnaces, which together with steel account for some 15 per cent of the present world's output, had originated in Germany during the 15th century and were introduced into England about 1500 A scarcity of wood charcoal gave the incentive which led, about 1620, to the use of coke obtained from pit-coal, and during the succeeding century, the use of this fuel became the established practice With improved types of blowing engines, following Watt's invention of the steam-engine, the blast furnace made huge strides

In addition to the effect of the high temperature carbonisation industry to meet the needs of the iron and steel trade, further impetus was given to the coal industry by the large-scale introduction of coal gas as a means of lighting and heating The coal gas industry dates back to the end of the 18th century when, in 1792, one William Murdoch illuminated his house at Redruth, Cornwall, with coal gas distilled in an iron retort During the early years of the 19th century, the gas industry made great strides in Europe, and later in America, and additional impetus was given by the invention of the Bunsen burner in 1855 and the incandescent mantle in 1885, both being discovered at Heidelberg, Germany

The foregoing summary briefly indicates the principal landmarks which directly and indirectly influenced the expansion of the coal industry during the period of industrial revolution at the end of the 18th and during the 19th centuries Time does not permit me to discuss in any detail the more recent developments, such as the vastly increased development in steam and electrical power, the production of producer gas and water gas, the use of pulverised fuel as such and in coal-oil mixtures, the manufacture of smokeless fuel by low temperature carbonisation and, latterly, the use of coal for the production of liquid fuels by hydrogenation

It is necessary to pass on and to give our attention to the *general* trend of events during the present century, and particularly since the War, in order to understand the position of the coal industry as it exists today

During the several decades before the War, the coal industry was expanding rapidly in this country, and with increasing industrialisation and demand, conditions were relatively smooth-running and prosperous Much the same thing was happening, though on a vastly larger scale, in Europe and America However, in spite of this relative prosperity, complications arose. With the rapid opening up of new mining areas without sufficient forethought to the question of a reasonable balance between output, prices, profits and wages, fluctuations in coal prices were bound to occur and conflicts between employers and workers naturally resulted, strikes occurring at intervals, often as a result of cuts in wages following falls in the sale prices of coal Thus the necessity of the integration, amalgamation and control of the industry became increasingly realised and, though many schemes were proposed without being put into execution, yet certain measures were adopted even before the end of the 19th century, and the period 1900–14 was characterised in many countries by the introduction of legislation regulating conditions of working underground, ameliorating to an important extent the lot of the unfortunate miner

As a result, when War broke out in 1914, some kind of equilibrium had been arrived at in the coal-mining industries of the various countries and to some extent in the international markets, though a great deal still remained to be done

The War naturally created a great disturbance in the industry Belligerent Powers experienced an internal shortage and could not meet the demands of foreign customers As a result, in spite of the opening of new mines in many countries, prices tended to soar To meet the situation, in practically all the belligerent countries, the coal industry was placed under Government control for stimulating production, rationing and fixing prices

As shipments from Europe to the Far East were cut off, the industry in Australia, China, Japan, South Africa and in this country expanded very appreciably, and a similar expansion occurred in the U S A in order to meet their enlarged industries and to supply certain European and South American countries In the case of the European neutrals, Sweden and Switzerland developed their water-power and Spain and the Netherlands their own deposits of coal Immediately following the War, in addition to the lasting effects of the changes that had taken place during 1914–18, further complications arose owing to political and economic developments

The boom of 1919-20, combined with various factors limiting production and export in certain important countries, all combined to produce a world coal shortage, giving rise to high prices, further mining development, a search for substitute fuels and progress in fuel economies

In 1921-22, an industrial depression followed, and coal prices collapsed

This post-War confusion, together with labour unrest, stimulated a widespread effort towards a comprehensive reform of the industry and coal commissions were set up in various countries Numerous proposals were suggested and a number were acted upon but the 'larger proposals for the nationalisation of the industry were not put into effect or, where enacted into law, resulted in arrangements which were far from the original intentions'

Relative world prosperity and industrial expansion succeeded during 1925–29 and this greatly assisted the coal industry, so that by 1927 the world production exceeded that of 1913 for the first time. Even so, during that period, the general *malaise* of the world coal-mining industry and the concept of a world 'coal problem' calling for international action began to gain ground Among the events, the 10 months' stoppage in Great Britain in 1926 assisted other European countries and the U S A temporarily, but with her return to the market the struggle in competition was renewed

Late in 1929, collapse again occurred and, combined with the substitution of other fuels for coal and as a result of increasing fuel economies, the production and consumption of coal fell to unprecedentedly low levels

In order to realise the nature and magnitude of the difficulties involved during the last few years we must momentarily retrace our steps to the events of the several preceding decades in addition to taking note of the happenings of the years succeeding the 1929 depression

Throughout the 19th century and until the War, the world demand for coal had developed at an average rate of 4 per cent per year

But between 1913 and 1937 this demand increased at a mean of only 3 per cent annually

During recent years, the factors tending towards a diminution of demand have, especially since 1929, appreciably exceeded in force the factors leading to expansion These post-War factors of contraction of the demand for coal include —

(*a*) the depressed state of the railways and steamship transport,

(*b*) displacement of coal as a fuel by mineral oils, natural gas and water-power;

(*c*) the production of a much greater proportion of the world's steel output direct from scrap iron than was the case in pre-War days,

(*d*) appreciably higher levels of fuel efficiency

There is not time to discuss these various factors, I will merely draw your attention to the following data.—

(1) Excluding the navies of the world, in which almost complete replacement of coal by oil has taken place during the past 25 years, the coal-fired vessels fell in tonnage from 44 million or 97 per cent of the world total in 1914, to 32 million or 49 per cent of the world total in 1937. During that period, oil-fired vessels expanded in tonnage more than 15 times over to about 20 million tons, and motor-ships by 13 5 million tons

(2) Regarding economies in the use of fuel the following statistics show the great influence of this factor on the coal trade during recent years

In the U S A., the average fuel efficiency of industrial manufacturing concerns and railway transportation rose between 1909 and 1929 by approximately 33 per cent and continued to rise, but at lower rates in subsequent years.

In Great Britain, in electricity undertakings an improvement of 55 per cent occurred in fuel efficiency between 1920 and 1935 In gas-production there was a saving of 10 per cent of coal In the case of blast furnaces, 2·06 tons of coke and coal were used to produce one ton of iron in 1913 as compared with 1 66 tons (of coke and coal) in 1936 In railway transportation there was an average increased thermal efficiency of 4 4 per cent between 1928 and 1934 alone Realising the magnitude of these industries, it is easy to visualise the great influence these economies had on the coal industry Similar economies were, of course, achieved in many other countries

Another important development affecting the balance within the industry in recent years has been the greatly increased output per man shift as a result of the rapid introduction of machine mining, an increase which has varied from 10 per cent in the case of Great Britain to over 100 per cent in the Netherlands

A further important development of the coal industry in recent years, to which reference must not be omitted, is the great expansion that has taken place in the output of coal in the U S S R From a production of 6 million tons in 1900, 36 million in 1913, and 48 million in 1930, rapid expansion resulted in an output of 126 million tons in 1936 and there is little doubt that during the past two years further increases have been recorded Fortunately, however, for the world coal trade, this rapid expansion added little to the problems affecting the industry as a whole, for the fuel produced was almost all consumed internally by the equally rapidly expanding home industries

In view of the above-mentioned trend of events, it is therefore not surprising to find that the world coal industry of the present century, and particularly of the past 10 years, has been and is still suffering from a large margin of surplus capacity for production and, it is believed, that this surplus capacity is at the root of the present coal problem ['Surplus capacity' is defined as 'the difference between the amount which existing mines, *without any additional investment of fixed capital*, could produce and the amount of actual output']

In 1929, the Economic Committee of the League of Nations came to the conclusion that, in European countries, there were margins of surplus capacity amounting to one-fourth in Germany, one-fourth to one-third in Great Britain and one-half in Poland

In the case of the output of bituminous coals of the U S A , the excess capacity was estimated to have risen from some 20 per cent in pre-War years to about 56 per cent in 1923. In 1929, it fell to 27 per cent, soared to over 90 per cent during the depression of 1932, and has more recently declined to about 46 per cent—the percentages being estimated as proportions of the actual output

It is, therefore, apparent that, since the War and particularly since 1929, the coal trade both in the home and in the world markets has suffered from a serious unbalance between power to supply and volume of effective demand.

This has, on the one hand, given rise to various schemes—both national and international—for the control of output and prices and for the general amalgamation and regulation of the industry, and has led many countries to take steps in an attempt to improve their individual positions The steps taken included the protection of the home markets by tariffs, etc , the granting of subsidies to encourage the export trade; manipulation of the national currency in foreign exchange and preferential trade agreements and bartering arrangements

Fortunately also, on the other hand, there has been progress towards international agreements as evidenced by the Anglo-Polish Coal Export Agreement of 1934, renewed with some modifications in 1937, and by the International Coke Cartel of 1937 allotting export quotas and fixing minimum prices in the case of the principal European exporters of coke—Belgium, Germany, Great Britain, Poland and the Netherlands The necessity for readjustment on a world-wide basis is, therefore, being increasingly realised and, it is to be hoped that, on the return to stable political conditions, further measures on these lines will be adopted in order that a return to a lasting period of stability and welfare for all concerned in the coal industry of the world will be forthcoming

HISTORY OF COAL MINING IN INDIA

By E R Gee, *M A (Cantab), F G S , Geological Survey of India*

India, in so far as the interests of those directly connected with her coal industry are concerned, is perhaps fortunate in being relatively free from the more complex problems of the world coal trade such as have existed and continue to exist in the European zone Being more or less a self-supporter in the matter of coal and, as a result of her location geographically, being in a position to resist any large invasion of her internal markets by imports from foreign countries, her coal industry has been allowed to develop steadily hand-in-hand with her general industrial expansion Whether this has been entirely to the country's advantage, and to the advantage of her coal industry in particular, is debatable, but this does not concern us at the moment

The coal-mining industry of India is a relatively recent development as compared with that of many European countries The first published reference to the mining of coal in India dates back to the year 1774, during the time of Warren Hastings, when permission to work coal mines in Bengal was accorded to John Sumner and Suetonius Grant Heatly As a result, mines, doubtless as open or incline workings, were reported to have been developed in the Raniganj field, at Aitura (Ethora) possibly in the Dishergarh seam, at Chinakuri near the Damodar river, doubtless in one of the middle Raniganj seams, and at Damulia, also near the Damodar, apparently in the Nega-Raniganj seam At least several thousand maunds[1] of coal were raised, of which some 2,500 maunds were delivered to Government in 1775. The latter reported it to be of poor quality As a result of various vicissitudes, this original adventure apparently ended in failure.

No further attempt was made to exploit coal in India for nearly 40 years, until 1814, when mining was commenced near Egara (Raniganj) Although this effort was again temporarily unsuccessful, sufficient interest was aroused to encourage further exploration and between 1820 and 1825 a number of mines were opened. Most of these were situated at no great distance from the Damodar river and exploited the seams of the Raniganj coal measures, particularly between Sitarampur and Chinakuri and near Raniganj Quarrying was also carried out in the upper Barakar seams near Chanch, to the west of the Barakar river.

The first systematic geological survey of the field was made during 1845-46 by Mr. D H Williams who was appointed Geological Surveyor to the East India Company, and a more detailed examination on the one-inch to one-mile scale by Dr W. T. Blanford during 1858–60 added greatly to our knowledge of the coalfield. By that time, some 50 collieries were already in existence

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[1] One maund = 82 pounds (approx).

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and during that period (1858–60) there was an annual average production of some 282,000 tons

In those early days, much of this coal was shipped to Calcutta in country boats which plied down the Damodar Since certain stretches of that river were navigable only during periods of high water, the journey was somewhat precarious and often took several months, whilst in many cases the boats were lost

One can, therefore, well imagine the encouragement given to the industry by the opening of the East Indian Railway from Calcutta to Raniganj early in 1855 and by its extension, during the next 10 years, westwards to Barakar and north-westwards *via* Sitarampur to link up with the system that was being developed over parts of the Gangetic plain

By 1868, the following five principal companies were engaged in winning coal in the Raniganj field and together they produced about 88 per cent of the total output of some 492,700 tons —Beerbhoom Coal Co, Ltd, Bengal Coal Co, Ltd, East Indian Coal Co, Ltd, Equitable Coal Co, Ltd, and Gobind Pundit, Siresol (Siarsol)

The detailed history of the development of mining in the field is, however, by no means a happy one and is typical of what happened elsewhere in India Government had not claimed the rights to the mineral wealth of the area and, therefore, would-be producers had to establish agreements on a royalty basis with the local land-owners Anyone acquainted with the question of the ownership of land in this country will realise only too well the complexities involved, and it is not surprising to find that many enterprises failed as a result of the expensive legal disputes which incessantly arose

During the earliest stages of coal mining in India, a certain number of miners had been brought from England These were, however, soon replaced by local labour working under European supervision

During the early stages of progress, exploitation was mainly from inclines and quarries but, as the years advanced, the number of pits of a depth of several hundred feet naturally increased, and with the extension of branch railway lines across the field, other areas were opened up

For the first century following the commencement of coal mining in India, the Raniganj field was the only, or at least the most important, producer. But towards the end of the 19th century, the large reserves of good quality coal of the Barakar measures in the Jharia field became increasingly realised. That area had been geologically examined by Mr T W. H Hughes of the Geological Survey of India in 1865, but mining development was not seriously taken up for a number of years

The 'rise' of the Jharia field has been dealt with by Dr Fox in a paper submitted to the Mining and Geological Institute of India in 1929 [see *Trans Min Geol Inst Ind*, Vol XXIV, pp 97–105, (1929)] and, as he points out, 'the whole future of the field in those days depended on railway communication'. Following an examination of the area in 1890, by Mr T. H Ward, Mining Engineer, East Indian Railway Company, the Grand Chord line was extended *via* Dhanbad to Katrasgarh by 1894 and during the following year the branch line to Patherdih was opened As a result, during the next decade, mining developed rapidly in Jharia and the output for 1906 exceeded the figure of 3,650,563 tons of the Raniganj field, and from that time to the present day Jharia has easily remained the principal producing field of India

Meanwhile, the relatively small, though important, Giridih or Karharbari field lying north of Jharia and some 23 miles west of the East Indian Railway main line had been receiving attention and mining had actually commenced as early as 1857 With the establishment of railway connection with the main line in 1871, the output of the good quality coking coal of this field increased rapidly, the East Indian Railway Company having the largest interest, a small production being derived from Bengal Coal Company mines By 1890, the total tonnage from the field had exceeded the ½-million mark and during the early years of the present century some ¾ million tons of coal were produced annually

Other coalfields in Bengal and Bihar, which were exploited during the latter half of the 19th century, included a small output totalling some 7,200 tons from the crushed Barakar measures of the Daling area in the outer Himalayas of the Darjeeling district, Bengal, between 1896 and 1900, and on a somewhat larger scale in the Rajmahal and Daltonganj areas of Bihar

Regarding these Bihar fields, coal was apparently mined at Rajhara in the Daltonganj coalfield as far back as 1842 and continued intermittently in a small way until 1931 In 1901, railway communication was established with the East Indian Railway main line *via* the Son Valley, prior to which date the coal had been despatched in boats down the North Koel river With the construction of the railway, the output increased in the early years of the present century to some 70 to 80 thousand tons annually

From the Rajmahal hills, an output of about 8,000 tons is recorded for as far back as the year 1858, and of some 28,000 tons and 45,600 tons respectively during the following two years After that, the output fell rapidly and ceased in 1863 for about a quarter of a century From 1890 onwards, small tonnages are recorded

The coal-bearing areas of central and southern India had been surveyed and reported on by the Geological Survey of India, principally by Hughes, William King and E J Jones, between 1860 and 1880 and, with the development of railways, attention was naturally paid to the possibilities of mining coal. In Central India, mining was commenced at Umaria in Rewah State in 1884 and a small production was raised from the Johilla field between 1898 and 1902 With railway facilities, the Umaria output expanded to nearly 200,000 tons in 1903.

In the Central Provinces, the earliest development of coal mining was, apparently, at Mohpani where a colliery was opened in 1862 by the Narbada Coal and Iron Co , Ltd With the construction of a railway connection about

1870, the output appreciably increased to some 40,000 tons in 1900 The collieries were purchased by the Great Indian Peninsula Railway Company in 1904

Further south at Warora, production commenced in 1874 and rose to a maximum of 153,336 tons in 1902 In 1906, the mines were abandoned as a result of underground fires

In Hyderabad State, the Singareni field was discovered by Dr William King in 1872, and the first raising took place some 15 years later Steady progress was made during the remainder of the century so that an output of 469,291 tons was reached by 1900

In north-eastern India, following earlier mining operations on a small scale, extensive developments took place in the Namdang and Ledo areas in Assam from 1881 onwards when a mining concession was obtained by the Assam Railways and Trading Company Communication with the Assam-Bengal railway was soon established and during the following 25 years the output of these Tertiary seams rose steadily to a quarter of a million tons annually

In the north-west, near Quetta, the mining of the relatively thin Tertiary seams was taken up on a small scale during the final decade of the last century, and was continued by the North-Western Railway Company for a number of years In the Punjab Salt Range, at Baghanwala, the working of a Tertiary seam, up to a few feet in thickness, was commenced by the same Company in 1893 and a maximum output of some 13,000 tons was raised in 1897 On account of the poor quality of the coal, the mines were closed down in 1899-1900 Other mines had previously been started (in 1884) in the adjoining Dandot area by this Company and a maximum production of 81,218 tons was raised in 1899 Since then the production declined and the collieries were handed over to contractors about 1911.

In the year 1900, the total production of these Punjab mines was only 74,083 tons

At Palana, near Bikanir in Rajputana, the mining of Tertiary lignites commenced on a small scale in 1898 and production rose to some 45,078 tons in 1904 since when it has declined

At the beginning of the present century the coal production of India had reached a total of about 6·1 million tons of which nearly 5 million tons were obtained from the Raniganj, Jharia and Giridih fields Blast furnaces had been in existence at Kulti in the Raniganj field for a number of years

Continued progress was made in Indian coal mining during the following pre-War period, a total output of nearly 16·5 million tons being produced in 1914, including about 9·15 million tons from Jharia and nearly 5 millions from the Raniganj field

During this pre-War period, the Bokaro (1908), Rampur (Ib River) (1913) fields in the north-east were opened up In the Central Provinces the Pench Valley (and Kanhan) fields commenced production in 1903 when the branch line running from Chhindwara was opened, and production rose to 95,679 tons in 1914. Still further south the Ballalpur field in Berar, also opened in 1903, increased its annual production to about 90,000 tons during the same period

Regarding the Tertiary fields, the production of Assam had risen from 216,736 to 305,160 tons during the same pre-War period, whilst in north-western India, including Rajputana, Kashmir, Punjab and Baluchistan, the total had risen from about 106,600 to a little less than 120,000 tons In the Trans-Indus Range of the Mianwali district, at Makarwal, small incline-workings were commenced in 1903 in the outcropping Eocene seam, but production was limited to a maximum of some 2,500 tons annually

During the War and in the year following, the demand for coal was naturally acute and a number of new collieries were opened up to meet the increased internal demand The total production rose to 22·6 million tons in 1919. The demand for coking coals was, about this time, appreciably enhanced by the construction of the iron and steel works at Tatanagar immediately preceding the War and the blast furnaces at Hirapur during 1922

During or immediately following this wave of increased prosperity a number of new fields were opened up including Jainti (1915) and Ramgarh (1920) in Bihar, Sohagpur (1921) in Central India, Ghugus (1920) and Shahpur (1921) in the Central Provinces and Sasti (1920) in Hyderabad State, whilst in northern India the output of Makarwal coal improved appreciably Prospecting work was being carried out in the Karanpura fields in Bihar and the Talchir field in Orissa, and production commenced during the 1923-24 period

The acute variations in the economic thermometer during the subsequent 15 years have, in India, as in the world as a whole, been reflected in the coal-mining industry of this country.

The marked trade depression of the 1920-21 period badly hit the coal-mining industry and a number of mines, particularly those exploiting inferior grade seams, were forced to close down, though during that period the deepest shafts of Indian coal mining—of a depth of 1,480 feet to the Dishergarh seam at Parbeliya—were completed During the year 1920, production fell to below 18 million tons and although it improved gradually during the following decade, yet prices continued to fall to a low level Conditions during the 1921 to 1923 period were further adversely affected by an adverse foreign trade balance in coal amounting to some 1,143,500 tons in 1922. At Mohpani, in the Central Provinces, production ceased in 1926 Another trade depression during the early part of the present decade, with still lower prices prevailing, further restricted enterprise, and resulted in the closing down of mining activities in certain of the smaller fields including the Rajmahal area, Hutar and Daltonganj.

Subsequent to 1933 an increased internal demand and a rapid rise of the foreign trade balance in India's favour, to a total of 808,460 tons in 1937, together with a decided improvement in the prices attainable at the pit's mouth since 1936, have brought more prosperous conditions to the coal-mining industry of India and the total output for 1938 reached the record of 28·3 million tons.

Largely on account of the fact that the majority of the seams worked in India are relatively thick, rarely less than 5 feet except in the case of certain of the Tertiary seams of north-western India, the pillar and stall method of working has been almost wholly in vogue In the case of the very thick coal seams, quarrying has of course been adopted at the outcrop

As has been stressed in recent years by a number of writers, the fact that at least in the two major fields the mineral rights of the very numerous surface land-owners have not been questioned, has often resulted in the working of certain of the most valuable seams from a very large number of small isolated mines in contrast to larger and more economically run collieries It is admitted that in a number of instances this has led to relatively inefficient methods of exploitation and to a much greater wastage in barriers separating the various concessions than would otherwise have been the case

Also, during the process of mining—until recent years—only in a very few cases was attention given to stowing Large reserves of coal were therefore left in pillars and as a result of subsequent fires originating from spontaneous combustion, a considerable proportion of this coal has been irretrievably lost It is unnecessary for me to go into this question in detail, the subject has been brought to our notice repeatedly in recent years and you are all aware of the relevant literature that has been published Suffice it to say, that there appears to be good prospects of a marked increase in stowing in the not distant future

Since the War, machine-mining has increased appreciably in India, but a very large proportion of the output is still won by hand

One cannot conclude a discussion of the history of coal mining in India without a reference to the associated bodies—the Department of Mines and the Mines Board of Health. The former was established in 1893 with its headquarters at Dhanbad A Circle headquarters exists in the Raniganj field

In a discussion on this subject, it is, I think, relevant to compare briefly the condition of the coal-mining industry in this country with that of the larger producing countries of the world Particularly in the case of western Europe, we have seen that severe internal and international competition has forced the industry to adopt measures of regulation and amalgamation that have led to greater efficiency and economy in the methods of exploitation, whilst the necessity of reaching agreement on the question of minimum prices and quotas has been increasingly realised. Though the difficulties impeding the adoption of similar measures in India are undoubtedly great yet they cannot be regarded as insuperable and it is to be hoped that, in the interests of the industry, a solution of these problems will be found in the near future.

THE GEOLOGY OF INDIAN COAL

By E R GEE, *M A (Cantab), F G S , Geological Survey of India*

If you look up two of the recent leading text-books on coal in general you will find that in one case it is recorded that the 'Indian Ocean' group of coalfields (including China, India, Australia and South Africa) 'are known to date from Upper Carboniferous times, although Permian coals are also known' whilst in the second text-book it is stated 'The coals of India are of earlier (Triassic) formation than the coals of Great Britain'

In so far as India is concerned, it may be safely stated that the Gondwana coals of economic importance are all of Permian age, they are located almost wholly in the peninsula But in addition, mainly in the mountainous tracts lying north of the peninsula, India possesses important deposits of Tertiary coal all of which belongs to the lower Tertiary (Eocene).

Past geological literature also refers to deposits of Jurassic coal in Cutch and in the Salt Range area of the Punjab Local occurrences of lignified wood and inferior coal are certainly met with in the variegated stage of the Jurassic of these areas and the coal has, in the past, been excavated on a very small scale near Kalabagh But the amount available is very small and analyses have shown it to be of poor quality Mr R R Simpson, in his account of the coalfields in India, published in 1913 (see *Mem Geol Surv Ind* , Vol 41, p 7), refers also to Cretaceous coal in Assam but more recent work by the Geological Survey of India in that area renders it probable that the latter are of lower Tertiary (Eocene) age

The coal-bearing strata of India, within which coal of economic importance exists, may therefore be classified under two main heads—the Gondwana (Permian) measures and the Tertiary measures

For a detailed account of the Gondwana coal measures of India, I would refer you to Dr. Fox's memoir on that subject [*Mem Geol Surv Ind* , Vol 59, (1934)]

Briefly, these coal measures and associated strata, all of which belong to the lower part of the Gondwana system, include in the main typical fresh-water deposits which were laid down in wide river valleys and lakes that traversed the Gondwana continent during Permian and later times The stratigraphical sequence involved includes:—

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Raniganj field	Jharia field	Central and southern fields.
- - -	(Panchet series)	- - -
Raniganj coal measures		Kamthi series
Ironstone Shales	Barren measures	,, (?)
Barakar coal measures.		
(Talchir series)		
[Archaean and pre-Cambrian basement]		

There is good reason to suppose that the whole of peninsular India and probably its extension northwards into what is now the site of the Outer Himalayas, at least for some distance east of Nepal, formed an ancient land-mass during the early and mid-Palaeozoic period To the north and north-west an extensive sea—the Tethys—existed, and into this sea a number of large rivers, draining in a general northerly direction, carried much of the sediment derived from the Indian portion of Gondwanaland This sediment went to form the fossiliferous marine Palaeozoic strata now met with in the inner parts of the Himalayan, Hindu Kush, and more northern ranges, and also in the Salt Range and in Baluchistan.

With the continued denudation of Gondwanaland to the south, this ancient land-mass was cut up into a series of wide valleys and lowland tracts and in these the fresh-water Gondwana strata were deposited Climatic conditions were apparently frigid during the latter part of the Carboniferous period so that the upland regions separating the low-lying areas were of sufficient altitude to support large ice-caps—the source of the glacial and fluvio-glacial conglomerates of early Talchir times, which form the basal strata of the Gondwana system in India With a change to a warmer climate, vegetation of the type now represented in our coal seams and in the well-known *Glossopteris* flora commenced to flourish on this ancient continent and spread rapidly with the progress of time As a result, during the early Permian, immense volumes of decaying vegetation were incorporated in the sand, gravel and clay debris that was eroded from higher levels, and these sediments were deposited overlying the Talchir strata in a number of the valley areas of Gondwanaland These lower Permian sediments including the accumulations of vegetation are represented in the Barakar coal measures as met with today. They comprise some 2,000 feet of felspathic sandstones, conglomerates, clays including fireclays, occasional ironstones and the majority of India's most important coal seams In most of the areas of deposition, seams of coal were probably included but, as may be well imagined from the varying nature of the conditions under which deposition took place, the thicknesses of the individual beds varied considerably from place to place

Regarding the conditions of formations, nowhere in India do we find definite evidence of a coal seam having been formed *in situ* as a result of the coalification of an ancient forest, on the other hand, there is plenty of evidence pointing to the drift theory of formation and it seems probable that, in at least the great majority of cases, the coal has been formed from accumulations of drift vegetation, carried down by the rivers and deposited in wide, low-lying areas of sluggish drainage.

In the case of the greater part of the area in question, conditions suitable for the accumulation of vegetable debris, to a sufficiently large extent to give rise to coal seams of workable thickness, ceased at the end of Barakar times and the succeeding strata include only sandstones, shales and ironstones

In the eastern part of the present Damodar valley region, however, a sequence of 'barren measures'—some 2,000 feet in thickness—was succeeded during Upper Permian times by a second series of coal-bearing strata, now represented by the Raniganj coal measures of the Raniganj and Jharia fields

Following the deposition of higher Gondwana strata—sandstones, clays and conglomerates, including plant-remains in many places—the Gondwana deposits of the Indian peninsula were dissected by numerous faults, in most cases of the normal type, during late Mesozoic times These faults varied in throw up to several thousand feet in a number of instances, displacements of at least 9,000 and 5,000 feet limiting the Raniganj and Jharia fields respectively on the south side As a result of this faulting, masses of the Gondwana strata were dropped down within the older—Archaean and pre-Cambrian—rocks and were thus to a large extent preserved intact from the effects of sub-aerial erosion during the subsequent Tertiary era

The Gondwana coalfields of India as we see them today, therefore, represent remnants of a coal-bearing sequence that was once much more widespread in its distribution.

In addition to faulting, the measures of the eastern part of the Damodar valley were intruded by a series of ultra-basic dykes and sills during the late Mesozoic These in many instances played havoc with the coal seams, resulting in the large quantities of 'jhama' with which we are acquainted only too well today A closely associated series of doleritic and basaltic dykes and sills were also intruded into the strata of peninsular India during late Mesozoic times. These intrusions, fortunately, had only a relatively limited effect on the coal seams

The stage of maturity reached by the Gondwana coals varies from matured bituminous in the case of the Barakar seams of certain of the western Damodar valley areas to less matured bituminous and sub-bituminous types in other areas and in the case of the Raniganj coal measures

The peninsular fields were apparently little affected by the intense earth-movements that gave rise to the Himalayan and related mountain ranges during late Tertiary times, but the extreme north-eastern part of the Indian portion of Gondwanaland was caught up in these movements, resulting in the sheared, coal-bearing Gondwana strata of the Daling field and adjoining areas.

As mentioned above, during a large part of the Palaeozoic and during the Mesozoic era the area north and north-west of Gondwanaland was submerged beneath a sea—named the 'Tethys'—which stretched eastwards from Europe *via* Persia and Baluchistan and continued further east into the Shan States The southern edge of this sea, during intervals of the Triassic and Jurassic periods, lay in the vicinity of what is now the Salt Range and Trans-Indus Ranges of the western Punjab As a result, in these regions the sediments deposited included not only marine fossiliferous strata but also sandstones and shales of estuarine origin Among these strata are to be found lignified fossil-wood, occasional pockets of coal and definite seams of coaly shale which pass locally into bands of impure coal But none, so far, have proved of economic significance

Towards the end of the Mesozoic, a large part of north-western India including the western Punjab and southern Kashmir was uplifted above sea-level This newly-formed land-area was in places eroded and, under the influence of sub-aerial weathering, a well-marked bed of bauxite and laterite was formed in a number of localities The latter marks the time interval between the Mesozoic and Tertiary eras Closely associated with this laterite during early Eocene (Ranikot) times, in the area west of the Indus river beyond Kalabagh, the Makarwal coal seam was formed Immediately following these events in the early Eocene, the sea again encroached across this northern India tract resulting in the deposition of foraminiferal limestones, marls, shales and subordinate sandstones of variable thickness Local, though in places fairly widespread, estuarine and marsh conditions once again broke into this marine sequence and resulted in the formation during late Ranikot and possibly lower Laki times, of the thin lignitic coal seam of the Salt Range and of Baluchistan and the thicker coal deposits of Jammu province, Kashmir, whilst in addition the lignites of Palana, Bikanir State, were laid down That these coals were, in many cases, deposited in areas very close to the sea-coast (in contrast to the Gondwana coal seams) is evidenced by the close association of foraminifera-bearing shales with the carbonaceous beds

In all these areas, during the succeeding stages of the Eocene, marine conditions prevailed during which thick limestone and shale deposits were laid down.

Late in the Eocene, the area in question was again largely uplifted above sea-level and, following a short period of erosion, the older strata were covered during middle and late Tertiary times by the vast thicknesses of lacustrine, fresh-water sandstones, clays and conglomerates of Nimadric (Murree and Siwalik) system.

Late Tertiary to sub-Recent earth-movements of organic type, culminating in the formation of the Himalayan, Sulaiman and associated ranges of northern and north-western India, together with the effects of rapid denudation, exposed the lower Tertiary and older strata as we see them today.

Turning to Assam, the geological evidence indicates that at least the western parts of that province formed a portion of Gondwanaland until Cretaceous times During a part of the Cretaceous, the Tethys—or a branch of that sea—encroached across this north-eastern portion of the Indian Gondwana continent and marine sediments were deposited, remnants of which are seen in the southern outcrops of the Assam plateau

As in northern India, uplift then recurred and the Mesozoic-Tertiary interval was marked by erosion and the local formation of lateritic deposits on the exposed land surface Again, as in northern India, coal-forming conditions immediately succeeded during lower Eocene (Ranikot) times in the Garo and Khasi hill areas and resulted in the formation of several seams of lignite, two of which are of definite economic importance It was these seams which were previously regarded as of Cretaceous age but Dr Fox, to whom I am indebted for the recent observations here recorded regarding the Assam coal measures, is of the opinion that they are all post-Cretaceous in age

Marine conditions followed, in south-western Assam, giving rise to the foraminiferal Sylhet limestone stage during later Eocene times This limestone stage includes bands of sandstone with carbonaceous horizons and the latter locally thicken to a 4- to 5-foot seam of coal, now worked near Cherrapunji

In Upper Assam, estuarine conditions prevailed during middle and upper Eocene times and gave rise to the important coal measures of the Ledo, Makum and adjoining areas Several coal seams, lignitic and relatively high in sulphur, of an individual thickness of as much as 40 feet in places, were formed

Following a break in sedimentation during the Oligocene, sedimentary deposition again set in during the middle and upper Tertiary resulting in an immense thickness of sandstone and shale strata

Towards the end of the Tertiary era, the above-mentioned orogenic movements that affected the whole of northern Indian and adjoining tracts, caused the uplift, folding and faulting of the Assam area also and, combined with the effects of denudation, the coal measures were exposed along the southern and south-western parts of the plateau and in the Upper Assam region

In most instances, these Eocene coals of India have not matured beyond the lignitic stage, but in parts of southern Kashmir, where the tectonic forces were locally more intense, semi-anthracitic coals have resulted.

INDIA'S COAL RESERVES.[1]

By M S KRISHNAN, *M A , Ph D , F N.I , Geological Survey of India*

INTRODUCTION

When the Coalfields Committee reported in 1920, it was keenly felt that the country should be in possession of facts regarding her resources in coal, though a rough idea was available at that time, as will be seen from the report on the Coal Resources of the World issued by the XIIth International Geological Congress of 1913 (Toronto session) This question was taken up by the Geological Survey of India, which constituted a party working under the direction of Dr C S Fox The greater part of the work was done by 1930 and the results published in a series of memoirs—one dealing with the Jharia field[2] by Dr Fox, a second on the Raniganj field[3] by Mr E R Gee and a third on the Gondwana fields[4] by Dr Fox A fourth memoir on the Tertiary coalfields is now understood to be nearing completion. The available data were presented, four years ago, by Sir L L Fermor, in a paper entitled 'India's coal resources'[5] Since then no new data have come to hand though the Coal Mining Committee of 1936-37 had occasion to review this question in its report[6]

Total and Workable Reserves

The total coal reserves of all the Gondwana areas, to a depth of 1,000 ft , have been calculated as 60,000 million long tons, as shown in column 1 of Table I This would include all coal, good and bad, and all seams down to a foot in thickness These quantities become considerably reduced if only workable seams are taken into account, *i e* those having a thickness of 4 ft or more and containing not more than 25 per cent ash on the moisture-free basis The results are given in column 2 of the same Table

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[1] Published by permission of the Director, Geological Survey of India.

[2] Fox, C. S.—The Jharia Coalfield, *Mem. Geol. Surv. Ind.*, LVI (1930).

[3] Gee, E. R.—The Geology and Coal Resources of the Raniganj Coalfield, *op cit.*, LXI (1932)

[4] Fox, C. S.—The Lower Gondwana Coalfields of India, *op cit.*, LIX (1935).

[5] Fermor, L. L.—India's Coal Resources. *Bull Indian Indus. and Labour*, No 54, *Rec. Geol. Surv. Ind.*, LXIX, pp. 336–352 (1935).

[6] Report of the Coal Mining Committee, Chapter VI, (1937).

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TABLE 1

Total and workable reserves

Coal-bearing area	Million tons	
	1	2
Darjeeling foothills and E Himalaya	150	20
Giridih, Deogarh and Rajmahal Hills	350	130
Raniganj, Jharia, Bokaro and Karanpura	25,000	10,000
Son valley—Auranga to Umaria-Sohagpur	10,000	2,000
Chhattisgarh and Mahanadi valley	5,000	1,200
Mohpani to Kanhan and Pench valleys	1,500	250
Wardha Godavari valley	18,000	6,400
TOTAL	60,000	20,000

Coal of good quality

Coal containing not more than 16 per cent ash on a moisture-free basis and occurring in seams 4 ft and over in thickness within a depth of 2,000 ft from the surface, will come under this category The estimates of such coal, according to Dr Fox, are —

TABLE 2

Good quality coal

Area	Million tons
Giridih and Jainti	40
Raniganj	1,800
Jharia	1,250
Bokaro	800
Karanpura (North and South)	750
Hutar, Johilla, Burhar	50
Kurasia, Jhilmili, etc	30
Talcher to Korba	200
Kanhan-Pench valleys	30
Ballarpur Singareni	50
TOTAL	5,000

Of this amount, 3,500 million tons occur within a depth of 1,000 ft, and the rest between 1,000 and 2,000 ft Sir Lewis Fermor has modified the figures for Bokaro and Karanpura and as a result gives a smaller total of 4,500 tons

It may be remarked, in passing, that some of the coalfields—*e g* those of Bengal, Bihar, Pench valley and Talcher—are being exploited intensively, and our knowledge of these is therefore more detailed and reliable than that of other fields Should it be possible to explore the less known fields fully by detailed geological mapping and by bore-holes, it is quite likely that the figures given above will be modified to an appreciable extent This applies particularly to the Wardha-Godavari valley and to the Satpura area Dr. Fox has summarised the available knowledge on the various areas in his memoir on the Lower Gondwana Coalfields and indicated where the data are meagre and where they are sufficiently satisfactory In any case, the estimates are well on the conservative side and any extension of our knowledge is almost certain to bring to light more reserves

Reserves of Coking Coal

A question which has been agitating the people interested in the metallurgical industries is that concerning the reserves of coking coal in India So far as our knowledge goes, coking coal of Lower Gondwana age is more or less confined to the Bengal and Bihar fields, especially Jharia, Raniganj, Giridih and Bokaro In Table 3 are given Dr Fox's estimates of good quality coking coal to a depth of 2,000 ft and Sir L Fermor's modification thereof

TABLE 3.

Reserves of Coking Coal

Field	Reserves (Million tons)		
	(Fox)	(Fermor)	(*a*) (*b*)
Raniganj	250	241	(73 + 168)
Jharia	900	900	(737 + 163)
Giridih	30	38	(38 + 0)
Bokaro	320	515	(270 + 245)
TOTAL	1,500	1,694	

(*a*) Down to 1,000 ft depth. (*b*) 1,000–2,000 ft depth

On the basis of information supplied by Dr E Spencer of Messrs Bird & Co, Sir Lewis Fermor has included about 350 million tons of the reserves of Karanpura under semi-coking coal which, when properly blended, may yield a suitable coke for metallurgical purposes

TABLE 4.

Good quality coal and coking coal reserves at the end of 1936

Area.	All good quality coal	Good quality coking coal.
Giridih and Jainti	22	20
Raniganj	1,763	230
Jharia	1,210	860
Bokaro	795	315
Karanpura (North and South)	750	
Hutar, Johilla, Burhar	50	
Kurasia, Jhilmili, etc.	27	
Talchir to Korba	198	
Mohpani, Kanhan-Pench	30	
Ballarpur-Singareni	45	
TOTAL	4,890	1,425

The Coal Mining Committee of 1937 had the opportunity of bringing these figures up to date (i e to the end of 1936), using Dr Fox's estimates as the basis (see p 62 of the Report) These are given in Table 4 Allowing for the depletion of the reserves during 1937 and 1938, the above figures will be reduced roughly to 4,850 and 1,400 million tons respectively

There are no published figures of the reserves of Tertiary coal, but according to Dr Fox the approximate figures are as follows.—

	Million tons
Upper Assam	1,000
Khasi and Garo Hills	1,000
Punjab, Kashmir, N W F P and Baluchistan	200
Bikaner	100
TOTAL	2,300

Having briefly reviewed our resources, it will be interesting to give a résumé of the knowledge of the coal resources of the world The International Geological Congress Report gave the total as 7,397,550,000,000 tons of which 69% was in North America, 17% in Asia, 11% in Europe, 2% in Oceania and barely 1% in South Africa and South America Table 5 is reproduced from 'The World Coal Mining Industry' (p 39) issued by the International Labour Office in 1938, which is itself a reproduction from the Statistical Year Book for 1933-34 of the World Power Conference As foot-notes to this table I have given the latest figures available for a few countries, the greatest divergence being noticeable especially in the case of China

TABLE 5.

World resources of coal and lignite

From I L O Report on World Coal Mining Industry, 1938, p 39, as quoted from Statistical Year Book for 1933-34 of the World Power Conference

(In millions of metric tons)

	Date of report	COAL.		BROWN COAL AND LIGNITE	
		Proved.	Probable	Proved.	Probable
Europe					
Austria	1930	13	19	611	2,337
Belgium	1913	*11,000 a*			•
Bulgaria	1934	1	1	500	1,000
Czechoslovakia	1932	6,450	25,000	12,500	
France	1935	6,000	17,000	1,600	1,600
Germany (A)	1922	80,440	279,500	28,837	56,758
Hungary	1932	200	200	1,550	1,550
Ireland	1934	107			
Italy	1913	1	146	51	100
Netherlands	1913	212	4,474 *b*		
Norway	1933		8,000 *c*		
Poland	1934	14,000	47,790	1,500	5,000
Spain	1913	4,500 *d*	5,500 *d*		
Sweden	1933	97	105		
U S S.R (B)	1933	295,900	998,000	12,890	202,000
United Kingdom	1933	129,500	176,000	•	
Yugoslavia	1913	2	33	58	250

TABLE 5—*contd.*

	Date of report	COAL		BROWN COAL AND LIGNITE	
		Proved	Probable	Proved	Probable
North America					
Canada	1913	30,319	242,400	391,260	572,686
United States	1928		2,040,640		852,128
Alaska	1913		3,554		16,560
South America					
Argentine	1933	0	50		
Chile	1913	2,116			
Peru	1919		1,000		
Africa					
S Rhodesia	1913	420	570		
S Africa	1927	7,914	205,682 *e*		
Belgian Congo	1913		100		
Nigeria (*g*)	1934	114	3,360		11,856
Tanganyika	1934	800	U		
Fr Morocco	1934	30			
Asia (D)					
China (C)	1913		10,112,000		
Manchuria	1913		1,129		
India	1932	5,000	20,600		
Brit Borneo	1934	0	0	3	13
Japan	1932	5,895	16,218	66	473
Chosen	1913		5,585		27
Australasia					
Australia	1927	20,900	139,400 *f*	10,620	U
New Zealand	1934	480	1,400	80	600

U—Not available (*a*) Within a depth of 1,500 metres (*b*) 'Actual, probable and possible reserves' (*c*) In Spitzbergen (*d*) Includes lignite (*e*) 'Proved, estimated and undetermined resources' of which 'proved and estimated' amount to 21,524 million metric tons (*f*) Large areas still remain unprospected and the figures do not include them (*g*) Includes Cameroons under British Mandate.

(A) 288,720 million metric tons of coal down to 2,000 metres (*Third World Power Conference*, 1936)

(B) Coal and Lignite in European U S S R 113,864 million metric tons, in Asiatic part 1,503,997 million metric tons (*17th International Geological Congress*, Moscow, 1937).

(C) 250,000 million metric tons (*Third World Power Conference*, 1936).

(D) Indo-China 12,000 million metric tons (*Min Met.*, p 333, July 1939).

INDIA AS A COAL PRODUCER [1]

By M S KRISHNAN, *M A, Ph D, F N I, Geological Survey of India*

WORLD PRODUCTION

The total world production of coal and lignite has been steadily growing since 1860, except during the last decade when the world witnessed an unprecedented economic depression The production during this period is given for a few representative years

Year	Million metric tons
1860	138
1870	236
1880	337
1890	513
1900	772
1910	1,165
1913	1,345
1923	1,359
1929	1,559
1936	1,446

The peak production was in the year 1929, but it is expected that it will be exceeded in 1938, though the final statistics for the latter year are not yet available

The output of the chief countries is given in Table 1 from which a general idea of the relative importance can be gained The United States, Germany, United Kingdom and U S S R are now the chief producers, followed far behind by a group comprising France, Japan, Poland, Belgium, India and China India thus occupies about the ninth or tenth place in order of importance. (See figure 1)

INDIAN PRODUCTION

Table 2 shows the output of the principal fields of India since the beginning of the present century. By far the largest part comes from the Lower Gondwana fields confined to eastern India in the Damodar-Son, Mahanadi and Godavari valleys and the Chhattisgarh and Satpura regions The Gondwana coal occurrences of the eastern Himalayan regions are of little or no economic importance. Amongst the Tertiary fields those in Assam are the most important.

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VOL. VI—No. 3. [Published August 15th, 1940.

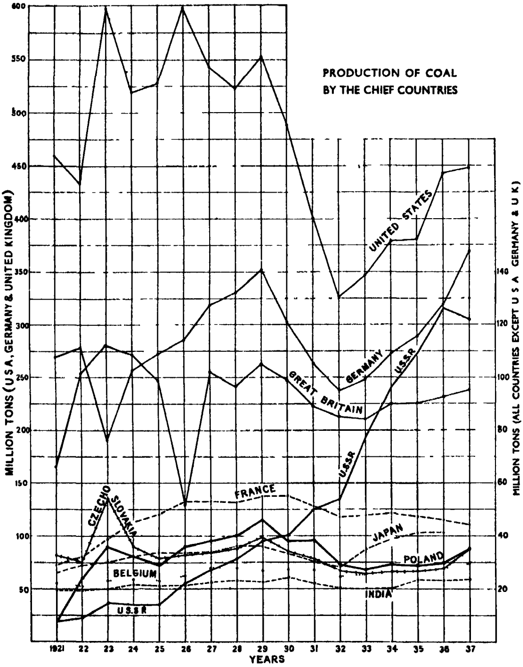
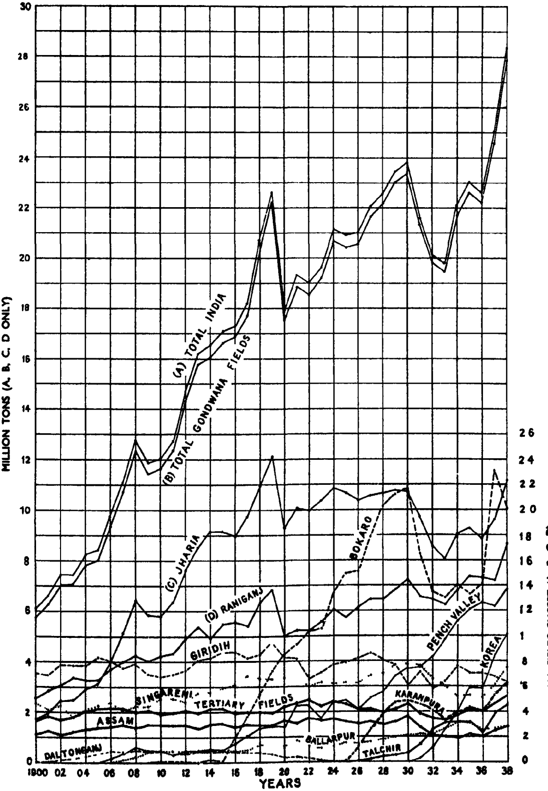


FIG. 1.

The aggregate output of the Tertiary fields was a little over 5 per cent of the total at the beginning of the century but it has dwindled to about 1·8 per cent at the present time (See figure 2.)

Of all the Indian fields Jharia and Raniganj are much the most important because of their large production and also because of their containing excellent coal and being the nearest fields to one of the largest consuming centres of India.



PRODUCTION OF COAL IN INDIA. BY FIELDS

FIG. 2.

TABLE 1.—*Production of Coal* (in million metric tons)

A—Anthracite, C—Bituminous Coal, L—Lignite

		1921	1922	1923	1924	1925	1926	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936	1937
U.S.A	A	82·1	49·6	84·7	79·8	56·1	76·6	72·7	68·3	67·0	62·9	54·1	45·2	44·9	51·9	46·3	49·5	46·2
"	C & L	377·3	383·1	511·8	438·8	471·8	520·1	469·7	454·3	485·3	424·1	346·6	281·0	302·7	326·0	335·0	393·8	401·4
Canada	C	10·7	10·6	12·2	9·1	8·6	11·7	12·3	12·4	12·3	10·4	8·5	7·5	8·5	9·6	9·4	10·3	11·0
"	L	3·0	3·2	3·2	3·2	3·3	3·2	3·4	3·5	3·6	3·1	2·6	3·1	3·4	2·9	3·2	3·5	3·3
S. America		1·3	1·1	1·2	1·5	1·4	2·1	1·9	2·0	2·0	2·2	1·8	1·8	2·2	2·5	2·8	2·6	2·9
Belgium		21·7	21·2	22·9	23·4	23·1	25·3	27·6	27·6	26·9	27·4	27·0	24·4	25·3	26·4	26·5	27·9	29·7
Czecho-slovakia	C	11·6	10·5	16·3	15·2	12·6	14·2	14·0	14·6	16·5	14·4	13·1	10·9	10·5	10·7	11·0	12·2	17·0
"	L	21·0	19·2	37·7	20·5	18·6	18·5	19·6	20·4	22·6	19·2	17·9	15·8	15·1	15·2	15·2	15·9	18·0
France		29·0	31·9	38·5	44·9	48·0	52·4	52·7	52·4	54·9	55·0	51·0	47·2	47·9	48·6	47·1	46·1	44·4
Germany	C	145·8	141·2	71·3	133·2	132·6	145·3	167·2	164·0	177·0	155·9	130·0	115·1	120·6	136·2	142·5	158·4	184·4
"	L	123·0	137·2	118·2	124·6	139·7	139·2	150·5	165·6	175·2	145·9	133·3	122·6	126·8	136·0	146·0	160·3	184·7
Hungary		6·4	7·1	7·7	7·2	6·3	6·6	7·0	7·2	7·8	7·0	6·9	6·8	6·7	6·9	7·5	7·9	9·0
Netherlands		4·3	4·9	5·6	6·4	11·3	10·0	9·7	11·1	11·7	12·3	13·0	12·8	12·6	12·4	12·0	12·9	14·4
Poland		7·8	24·2	36·3	32·2	29·1	35·8	38·2	40·7	46·3	37·5	38·2	28·8	27·3	29·2	28·6	29·8	35·2
U S.S.R.		7·5	8·9	14·5	13·9	14·3	22·2	27·6	30·6	38·4	39·9	50·4	53·6	77·7	96·2	109·0	126·0	122·6
Spain		5·4	4·7	5·3	6·5	6·5	6·9	7·0	6·8	7·4	7·5	7·5	7·2	6·3	6·2	7·3		
United Kingdom		165·8	253·6	280·4	271·4	247·0	128·3	255·2	241·2	262·0	247·8	223·0	212·1	210·4	224·3	225·8	232·1	236·9
India		19·5	19·3	20·0	21·5	21·2	21·3	22·4	22·9	22·5	24·2	22·0	20·5	20·1	20·4	23·4	23·0	23·7
China		19·9	22·7	18·6	21·0	21·2		18·3	25·1			27·7	28·0	28·4	32·7	26·8	27·1	
Japan		26·0	29·1	30·7	32·0	33·5	33·7	33·4	35·9	36·1	33·5	30·0	28·2	34·7	38·7	40·9	41·2	.
South Africa		10·3	8·8	10·8	11·8	12·3	12·9	12·6	12·6	13·0	12·2	10·9	9·9	10·7	12·2	13·6	14·8	15·5
Australia		13·1	12·5	12·9	14·1	14·7	14·5	15·2	13·6	12·3	11·0	10·7	11·3	11·8	12·6	13·3	14·6	15·6
World Total		1,134	1,226	1,359	1,357	1,372	1,365	1,470	1,464	1,559	1,413	1,258	1,124	1,176	1,284	1,329	1,446	1,515

TABLE 2 —*Output of coal in India by the principal fields* (in thousands of long tons)

	1900	1901	1902	1903	1904	1905	1906	1907	1908	1909	1910	1911	1912	1913	1914	1915	1916	1917	1918	1919
Jharia	1,711 28·0	1,947 29·8	2,421 32·6	2,494 33·5	2,890 35·2	3,071 36·5	4,077 41·7	5,179 46·5	6,459 50·6	5,833 49·1	5,795 48·1	6,874 50·1	7,653 52·0	8,608 53·1	9,147 55·6	9,141 53·4	8,950 51·9	9,784 53·7	10,952 52·8	12,146 53·7
Raniganj	2,552 41·7	2,842 42·8	3,042 41·0	3,067 41·3	3,350 40·8	3,263 38·8	3,651 37·3	3,981 35·7	4,222 33·1	4,035 34·0	4,213 34·9	4,312 33·9	4 944 33·6	5,327 32·9	4,946 30·0	5,485 32·1	5,535 32·1	5,376 29·5	6,369 30·7	6,815 30·1
Bokaro										2	3	*	8	3	17 0·1	10 0·1	197 1·1	361 2·0	542 2·6	723 3·2
Giridih	713 11·6	695 10·5	777 10·4	767 10·3	773 9·4	829 9·8	803 8·2	750 6·7	782 6·1	705 5·9	679 5·6	704 5·5	731 5·0	807 5·0	825 5·0	873 5·1	860 5·0	824 4·5	847 4·1	950 4·2
Pench valley				*		1 0·3	32 0·7	75 0·9	120 0·8	92 0·7	88 0·7	63 0·5	91 0·6	90 0·5	96 0·6	103 0·6	155 0·9	205 1·1	267 1·3	285 1·3
Singareni	469 7·6	421 6·3	455 6·1	363 4·9	420 5·1	454 5·4	468 4·8	414 3·7	444 3·5	443 3·7	506 4·2	505 4·0	482 3·3	552 3·4	556 3·4	587 3·4	615 3·7	681 3·7	659 3·2	662 2·9
Daltonganj (Korea from 1930)	1	4	19 0·2	34 0·5	51 0·6	71 0·8	87 0·9	82 0·7	96 0·8	84 0·7	85 0·7	71 0·5	72 0·5	85 0·5	82 0·5	86 0·5	76 0·4	77 0·4	82 0·4	63 0·3
Karanpura																				
Talchir																				
Ballarpur					*	*	1	18 0·2	45 0·3	85 0·7	93 0·8	97 0·8	86 0·6	81 0·5	89 0·5	95 0·6	85 0·5	95 0·5	135 0·7	126 0·6
Assam	217 3·5	254 3·8	221 3·1	239 3·2	267 3·3	277 3·3	285 2·9	296 2·7	275 2·2	306 2·6	297 2·5	295 2·3	297 2·0	271 1·7	305 1·9	311 1·8	287 1·7	301 1·7	294 1·4	292 1·3
Total Gondwana	5,785 94·6	6,265 94·4	7,083 95·4	7,076 95·1	7,808 95·0	7,093 94·9	9,349 95·6	10,720 96·2	12,373 96·9	11,463 96·6	11,636 96·6	12,329 97·0	14,298 97·2	15,814 97·6	16,039 94·4	16,673 97·5	16,863 97·7	17,815 97·8	20,323 98·1	22,239 98·3
Total Tertiary	334 5·4	371 5·6	341 4·6	362 4·9	409 5·0	424 5·1	434 4·4	427 3·8	397 3·1	407 3·4	412 3·4	386 3·0	408 2·8	394 2·4	425 2·6	431 2·5	391 2·3	398 2·2	400 1·9	389 1·7
Total India	6,119	6,636	7,424	7,438	8,217	8,418	9,788	11,147	12,770	11,870	12,047	12,716	14,706	16,208	16,464	17,104	17,254	18,218	20,722	22,628

	1920	1921	1922	1923	1924	1925	1926	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936	1937	1938
Jharia	9,294 51·7	10,069 52·2	9,936 52·3	10,346 52·6	10,846 51·2	10,677 51·1	10,374 49·4	10,583 47·9	10,065 47·3	10,786 46·1	10,754 45·2	9,756 44·9	8,551 42·4	8,015 40·5	9,058 41·1	9,246 40·2	8,840 39·1	9,601 38·4	11,144 39·2
Raniganj	4,998 27·8	5,212 27·0	5,203 27·4	5,557 28·3	6,035 28·5	5,730 27·4	6,125 29·2	6 472 29·3	6,460 28·7	6,828 29·2	7,219 30·3	6,531 30·1	6,419 31·9	6,266 31·7	6,796 30·8	7,348 31·9	7 305 32·3	7,196 28·7	8,651 30·5
Bokaro	858 4·8	929 4·8	1,037 5·5	1,060 5·4	1,344 6·3	1 405 7·2	1,515 7·2	1,791 8·1	2,027 9·0	2,119 9·1	2,160 9·1	1,657 7·6	1,349 6·7	1,305 6·6	1,399 6·3	1,331 5·8	1,417 6·3	2,309 9·2	2,007 7·1
Giridih	831 4·6	819 4·2	659 3·5	714 3·6	769 3·6	787 3·8	819 3·9	855 3·9	804 3·6	771 3·3	614 2·6	718 3·3	583 2·9	636 3·2	761 3·5	709 3·1	698 3·1	675 2·7	636 2·2
Pench valley	279 1·6	449 2·3	453 2·4	346 1·8	474 2·2	486 2·3	417 2·0	506 2·3	550 2·5	680 2·9	740 3·1	750 3·5	832 4·1	978 4·9	1,118 5·1	1,214 5·3	1,259 5·6	1,234 4·9	1,369 4·8
Singareni	666 3·7	646 3·4	604 3·2	629 3·2	620 2·9	630 3·0	610 2·9	682 3·1	699 3·1	768 3·3	765 3·2	658 3·0	593 3·0	519 2·6	528 2·4	513 2·2	606 2·7	741 3·0	691 2·4
Daltonganj (Korea from 1930)	39 0·2	37 0·2	32 0·2	12 0·1	4	17 0·1	10		1	Korea	4	31 0·1	114 0·6	264 1·3	400 1·8	590 2·6	580 2·6	851 3·4	1 013 3·6
Karanpura						13 0·1	124 0·6	262 1·2	390 1·7	467 2·0	482 2·0	462 2·1	410 2·0	344 1·7	397 1·8	425 1·8	396 1·8	534 2·1	626 2·2
Talchir				5	5	7	13	23 0·1	38 0·2	47 0·2	69 0·3	142 0·7	254 1·3	317 1·6	307 1·4	309 1·3	224 1·0	392 1·6	448 1·6
Ballarpur	128 0·7	171 0·9	133 0·7	112 0·6	128 0·6	150 0·7	143 0·7	159 0·7	176 0·8	202 0·9	212 0·9	223 1·0	217 1·1	256 1·3	321 1·5	313 1·4	247 1·1	264 1·1	279 1·0
Assam	326 1·8	312 1·6	348 1·8	326 1·7	335 1·6	319 1·5	301 1·4	323 1·5	298 1·3	323 1·4	359 1·5	275 1·3	210 1·1	194 1·0	190 0·9	221 1·0	203 0·9	249 1·0	278 1·0
Total Gondwana	17,526 97·6	18,844 97·6	18,520 97·4	19,217 97·8	20,696 97·8	20,447 97·8	20,583 98·0	21,664 98·1	22,153 98·3	23,002 98·2	23,342 98·1	21,332 98·2	19,815 98·3	19,456 98·3	21,691 98·3	22,607 98·2	22,212 98·2	24,571 98·1	27,824 98·2
Total Tertiary	436 2·4	459 2·4	490 2·6	440 2·2	478 2·3	456 2·2	416 2·0	418 1·9	390 1·7	417 1·8	461 1·9	385 1·8	339 1·7	332 1·7	366 1·7	409 1·8	398 1·8	405 1·9	519 1·8
Total India	17,962	19,303	19,011	19,657	21,174	20,904	20,999	22,082	22,542	23,419	23,803	21,716	20,153	19,789	22,057	23,017	22,611	25,036	28 343

The first figure against each field is the tonnage and the second the percentage of total Indian production. An *asterisk* signifies a production of less than 1,000 tons.

TABLE 3.—*Output of Coal in Countries around the Western Pacific and Indian Oceans* (in thousands of metric tons)

(Data taken from the League of Nations Year Books)

		1926	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936
Japan	L	161	179	148	139	129	118	109	116	127	109	109
,,	C	31,427	33,531	33,860	34,258	31,376	27,987	28,053	32,524	35,925	37,762	41,803
Br. Borneo		93	80	80	73	74	48					
Manchuria		8,139	8,960	9,477	9,924	10,041	7,049	7,099	9,063	10,704	11,474	12,020
Chosen		683	710	816	938	884	936	1,104	1,307	1,689	1,999	2,282
Sakhalin (Japan) ..	.	245	357	539	636	645	638	677	889	1,197	1,516	2,075
Formosa		1,795	1,800	1,584	1,530	1,599	1,422	1,355	1,533	1,521	1,597	1,744
Fr. Indo-China	..	1,290	1,486	1,967	1,972	1,955	1,726	1,714	1,591	1,592	1,775	2,186
Netherland Indies		1,466	1,620	1,704	1,832	1,871	1,404	1,050	1,035	1,033	1,111	1,147
Philippines		29	23	28	17	21	19	18	16	23		25
F.M.S. .		472	470	566	672	575	409	282	222	327	383	511
China	..	15,045	14,182	15,364	15,186	15,832	17,995	18,858	18,802	20,897		
India .		21,336	22,436	22,905	23,795	24,185	22,065	20,477	20,107	22,411	23,386	22,974
ASIA (ex. U.S.S.R.)		82,020	85,655	88,890	90,833	89,058	83,698	80,687	87,089	97,319	102,500	108,000
South Africa	.	12,950	12,580	12,607	13,018	12,223	10,881	9,921	10,714	12,195	13,574	14,842
S. Rhodesia		874	909	1,095	1,037	939	587	438	484	643	695	705
TOTAL AFRICA		14,258	13,961	14,182	14,535	13,667	11,914	10,693	11,510	13,190	14,640	15,921
Australia	L	973	1,479	1,617	1,769	1,861	2,230	2,654	2,621	2,660	2,257	3,094
,,	C	13,488	13,740	12,030	10,532	9,684	8,536	8,724	9,238	9,504	11,063	11,553
New Zealand ..	L	1,060	1,093	1,105	1,187	1,178	1,197	928	993	1,248	1,311	1,302
,,	C	1,215	1,312	1,370	1,389	1,405	995	943	857	845	838	873
TOTAL OCEANIA	.	16,751	17,633	16,139	14,898	14,138	12,958	13,249	13,709	14,257	15,469	16,822

L—Lignite, C—Coal.

There is a small production in Nigeria, Belgian Congo, Algeria, French Morocco and New Caledonia, these are included under the totals for Africa and Oceania.

In Table 3 are shown the output of countries on the Indian Ocean and Western Pacific sea-boards which are India's actual or potential competitors At present, South Africa is a keen competitor of India not only in her foreign markets but also often in parts of her domestic market A point worthy of note is that Indo-China is a producer of excellent anthracite which finds a ready market not only in China and Japan but also farther afield In fact Canada took more than 85,000 tons of Indo-China anthracite in 1937.

GENERAL TRENDS IN COAL PRODUCTION

Taking the world production of bituminous coal and anthracite for the decade 1926–35, the average annual figure comes to about 1,234 million metric tons The International Labour Office has calculated that, at that constant rate, the world reserves will last for about 37 centuries (World Coal Mining Industry, 1938, p 40) Table 4, reproduced from the above-mentioned publication, shows the reserves of a few important countries and the calculations of life based on different assumed rates of production

TABLE 4 —*Probable life of coal reserves*

Country	Reserves to 2,000 metres depth	Average annual production 1925–35	Probable life		
			At constant production	With yearly increase of	
				0 5%	2%
	Million metric tons		Years		
World	4,600,000	1233 5	3,730	595	217
United States	1,975,000	535 8	3,686	593	217
U S S R.	1,075,000	30 3	35,478	1,037	330
Great Britain	200,000	230 3	868	329	147
Germany	289,000	148 1	1,951	470	186
Poland	138,000	37 8	3,651	590	216
Canada	286,000	11 3	25,310	969	314
China	220,000	16 5	13,330	842	282

There are now more than 50 different countries which figure in statistics as coal producers Taking the coal output of the world in 1936 at 1,280 million metric tons (all kinds converted to a standard bituminous type on the basis of calorific value), this would be equivalent to 87 7 per cent of bituminous coal, 7·6 per cent anthracite and 4·8 per cent lignite.

It is an interesting fact that the production of coal in 1913 was about the same as in 1936, though there has been considerable change in the contribution of different countries towards this total. For instance, U S A and Great Britain produced nearly two-thirds of the total in 1913 whereas they were responsible for only half the total in 1936. In 1913 the aggregate production of Russia, Japan, China, India and South Africa was only 7 per cent of the total while in 1936 their contribution rose to about 17 per cent. The Soviet Union has forged its way to the front rank during the last decade or so.

At present over three-fourths of the world production (of coal equivalent) is from four countries, and over nine-tenths by ten countries as will be seen from the percentages of output in 1936 —

	Per cent		Per cent
U S A	34·4	Czechoslovakia	1·7
Great Britain	18·1	China	1·6
Germany	15·2	S Africa	1·2
U S S R	8·7	Netherlands	1·0
France	3·6	Manchuria	0·9
Japan	3·0	Australia	0·9
Poland	2·3	Canada	0·9
Belgium	2·2	Others	2·5
India	1·8		

It will thus be seen that the production is still greatly concentrated in a few countries which have made rapid progress in the mechanised industries. Still more striking is the fact that a small group of fields in the world (Table 5) is responsible for a very large part of the output.

TABLE 5.—*Production by the chief districts in 1936*

District	Million tons (Coal equivalent)	Percentage of world output
West Virginia (U S A)	106·6	8·3
Pennsylvania ,,	98·6	7·7
Penn anthracite ,,	49·8	3·9
Illinois ,,	45·6	3·6
E Kentucky ,,	35·6	2·8
Indiana Iowa ,,	19·1	1·5
Ruhr-Aachen (Germany)	115·1	9·0
U and L Silesia ,,	26·2	2·0
Central lignite fields ,,	15·2	1·2
Saar ,,	11·7	0·9
East Upper Silesia (Poland)	22·1	1·7
Donetz (U S S R)	75·2	5·9
Kusnetz ,,	17·3	1·3
South Wales (England)	34·4	2·7
Durham ,,	31·9	2·5
S. Yorkshire ,,	30·7	2·4
Pas-de-Calais-Nord (France)	28·5	2·2
Charleroi-Mons (Belgium)	11·9	0·9
Bengal-Bihar (India)	19·1	1·5

The gradual shift that is taking place in production is to be attributed to a large extent to the growth of industrialisation. Other factors affecting the consumption of coal are advances in fuel efficiency and the displacement of coal by petroleum and water-power.

Though coal figures as one of the most important mineral products, only 10 per cent of the world production enters into world trade, for the producers are also important consumers Countries deficient in coal try to develop water-power as in the case of Scandinavia, Switzerland and Italy

There is every indication that production will go on rising in many countries, depending on the extent of their coal resources and rate of development of industries This is particularly true of the newer industrial countries of Asia and Africa

CONSERVATION OF COAL[1]

By M S KRISHNAN, *M A*, *Ph D*, *F N I*, *Geological Survey of India*

The term 'conservation' as applied to any assets connotes their preservation In the case of irreplaceable or wasting assets like minerals it can only mean the avoidance of waste in all phases of handling, and the careful and wise utilisation of the deposits The conservation of coal will therefore necessitate careful control of mining, processing, beneficiation, transport, distribution and industrial use True conservation will not be attained unless every one connected with any phase of winning, trade and utilisation of the mineral takes steps to see that no waste takes place

Reserves

The first step towards conservation is the acquisition of knowledge of the available resources of the country As dealt with in another paper in this symposium, conservative estimates show that India possesses about 20,000 million tons of workable coal within a depth of 1,000 feet from the surface Good quality coal (*i e* coal with less than 16 per cent ash on a moisture-free basis) amounts at present to about 4,850 million tons within a depth of 2,000 feet. Of this again, only about 1,400 million tons are good coking coal This inventory is a good approximation to truth on the data available at present With more detailed data and the inclusion of seams thinner than 4 feet in the estimate, appreciably larger reserves may be available

Life of the reserves

A certain definite proportion of the reserves is not mineable since some waste is unavoidable in mining Peculiarities of structure and composition, faulting, crushing, proximity to igneous intrusives, etc have all some influence on mining and on the amount that could usefully be recovered Hence calculations of the life by a simple division of the reserves by the present or estimated future consumption will be falsified by a large margin

Best material usually worked first

There is also the natural human tendency to get at the best material first and exhaust it before any serious thought is given to the poorer qualities available The exploitation of all minerals in all countries has been, and still is, subject to this tendency. If the best seams are worked first, parts of these and much of the less attractive material in the contiguous strata become spoilt

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[1] Published by permission of the Director, Geological Survey of India.

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or even unworkable at a later date, unless special precautions are taken in due time The less accessible areas are naturally left over for future exploitation Thus, as the market demand steadily mounts up, the price of the commodity also goes up because of the higher expense of mining at depth and of the greater difficulties to be overcome, and also the longer haulage to the consuming centres

We are quite familiar with the phenomenon of the ordinary consumer in India buying coal by the name or the number of the seam which has an established reputation on the market, rather than on analysis and other scientific criteria This leads to the continued exploitation of particular seams while the others may suffer simply because they are not sufficiently well known Again when part of a seam is of high quality, only that portion is worked while the rest is neglected and not infrequently wasted

Incidence of freight

In a large country like India with a limited geographical distribution of the coalfields, the cost of transport becomes an important and often the paramount consideration Thus, Lahore or Peshawar has to pay, in freight, five or six times the pit's mouth value of the coal from Bihar. Places west of Nagpur have often to be content with the second grade coal produced in the Central Provinces because the cost of Bengal or Bihar coal is double or treble that of the local coal In the fields producing different grades, the demand is generally brisk only for the best grades, unless price differences are sufficient to encourage the use of lower grades or unless research has proved that certain particular types are best suited for specific uses

Underground mining

Underground mining in India involves at present a heavy loss of coal in the seams It was estimated by the Coal Mining Committee of 1936-37 that only 60 per cent and 50 per cent respectively of the coal in pillars in the Raniganj and Jharia fields is being recovered at present This would mean that roughly 25 to 40 per cent of the original coal in the seams is irretrievably lost under the present methods of working

Disadvantages of deep mining

In some European countries it has been found necessary to work seams 3 feet or less in thickness, because thicker seams have already been worked out or are not able to meet all the demand In Belgium, for instance, some seams barely 20 inches (51 cm) thick, and having comparatively high dip, are being worked at a depth of nearly 4,000 feet Such conditions involve high engineering efficiency, costly mechanical equipment, and high maintenance and labour costs concomitantly with less production per man-shift, all these factors inevitably increasing the cost of the commodity. In the above instance, the output per man-shift is only about 1 ton, whereas in working seams of 6 to 7 feet thickness under moderate depths with the same mechanical facilities the output is 4 to 5 tons Though we, in India, are still far from the period when thinner and inferior seams will regularly have to be worked, it would be well to recognise and emphasise the evils of prodigality in the early stages of intensive exploitation and be forewarned about the future

Geological factors

The geological structure of the seam and the nature of the floor and roof limit the recovery to some extent Coal has often to be left in the roof, especially of thick seams, and where the roof is weak, also in panel walls, pillars and boundaries, and around the shaft bottom It has also to be left to support surface structures, railways, roads, stream beds, etc Local patches of low quality and undulations or rolls in the seams are also sources of loss It has been pointed out by the Coal Mining Committee that some portions of the seams which are worked for export are of low grade and are not worked In this case, part of the responsibility for ultimate loss rests upon the State since it is prohibited by law to work the ungraded and graded coals at the same time As a general statement it is true that only the best and cheapest worked coal is mined and an appreciable portion of the reserves is left behind and lost at least in part Such loss is undoubtedly 'avoidable waste' and militates against conservation

Mining methods

The system of mining has to be adapted to the peculiar local conditions in the field and the structure of the seams in order to avoid losses to a minimum Since the seams are thick in India and the mining system followed is the 'pillar and stall', the question of pillar extraction presents great difficulties unless adequate measures are taken for the support of the roof The measures now being taken by the Government of India for the enforcement of universal sand-stowing will go a long way towards the realisation of conservation

Machine mining

It may be mentioned in this connection that mechanisation of mining operations is not always conducive to the avoidance of loss. Certain types of equipment (*e g* face conveyor and scraper) permit of mining thin seams with high recovery If, however, the seam contains layers of poor quality, machine mining cannot be as discriminating as hand mining, with the result that the grade of coal is brought down or an appreciable part of the better portion of the seam is left behind Under certain circumstances, therefore, mechanical mining is much less flexible than hand mining

Labour

Increasing efficiency of labour and the use of labour-saving devices will make for lower cost of production, and incidentally greater safety. Labour is cheap in India but comparatively inefficient, but there is no reason why it could not be trained to better efficiency The proper observance of mining rules and regulations depends ultimately on intelligent and responsible labour, and though mining regulations aim primarily at safety they also indirectly aid in conservation

Reopening of abandoned mines

Private agencies can function only so long as there is a reasonable prospect of profit Since industries in most countries are sensitive to fluctuations and vagaries of trade, premature abandonment of mines (*i e* with partial recovery of coal) is fairly common Once a property is partially worked and then abandoned, it is difficult to reopen it, for this would involve heavy additional expenditure in pumping, reconditioning, support, etc In several cases it is quite uneconomic to reopen such properties and try to recover the unmined coal.

Rehabilitation of the surface

Finally, mined areas often present a desolate and ruined aspect, caused by collapses and fires This is already assuming appreciable proportions in some of our important coalfields We can also imagine what the large open-cast mines in the Bokaro field will look like when finished with The collapsed and mined areas could profitably be repaired and re-graded so that they could be afforested or made fit for agricultural purposes

Some economic aspects

In countries which do not exercise much control over the industry, the market is highly competitive, and the producers naturally want to mine the coal as cheaply as possible Such conditions generally encourage waste It then becomes the duty of the State to enforce certain necessary steps for the prevention of waste, ensuring at the same time that no class of producers suffers a handicap thereby in comparison with others This means inevitably a slightly higher cost of production which will be passed on to the consumer, but this sacrifice on the part of the latter becomes a national necessity For, if the consumer is reluctant to pay a little higher price now, he will be forced to pay a much higher sum in future for a distinctly inferior product Under good and efficient management it is possible to obtain a higher recovery of coal without material increase in cost, within limits The complete recovery of pillars and roof coal, however, generally means extra cost, but there is the countervailing advantage that a larger tonnage is recovered from the same mine, there being some savings in certain items of cost such as the general equipment, ventilation, haulage, etc. The land-owner gets more money as royalty from the same property, as also the taxing authorities. The charges for depreciation of the value of the mining property are spread over a longer period and over a larger tonnage of output

These considerations will apply in varying degrees to different properties In the case of the very long leases of the early days which were given under extremely cheap rates—*e g* some of the very early leases given by the Permanent Settlement landlords of Bengal and Bihar—it may not be at all profitable for a concern to work the small amount of extra coal On the other hand, certain items are always more costly, such as de-pillaring, timber supports and labour Considering all the factors, however, the extra cost per ton spread over the whole of the resources of the mine will be very small and will not seriously affect the market price in most cases

The steady or intermittent nature of the operations has an important effect on cost, since a steady output is always conducive to better planning, ordered development and lower costs

Regarding the effect of complete recovery of coal on surface subsidences, there should not be a great deal of difference between partial recovery and complete recovery, for even if pillars are left to support the surface, they tend to become crushed in time and produce sags and cracks. Unless there are costly structures on the surface, the expense of re-grading the surface for agricultural purposes will not tell seriously on the cost of recovery of the coal which would otherwise be left unworked

Much the most important obstacle to complete recovery is the keen competition in an uncontrolled market Unless it is made worth while for the lessee to win the extra coal, *i e* unless there is a market for the extra coal, which may be sometimes of a low grade, it will be impossible to induce him to take the trouble of mining it It is therefore imperative that the question of the additional cost involved should be studied in all its aspects and measures adopted to enable the industry to take the necessary steps for ensuring conservation In the last analysis, this will necessitate not only production control but also price control

Excess capacity is a common feature, at the present day, of the mining and manufacturing industries of many countries, particularly of those which have had an early start in industrialisation It also happens that an enormous impetus is given to the increase of productive capacity during times of crises like wars, but generally no steps are taken to reduce the capacity to normal as soon as the crisis passes Thus overproduction lingers on with its attendant disability—price cutting and cut-throat competition Control of production is the only remedy for this state of affairs

Conservation in preparation and use.

Great progress has been made in recent years in the preparation of the coal for the market by sizing and cleaning Sizing enables the consumer to use the material straight in the form in which it is delivered to him and which suits his purpose best. Sizing of the product is an essential operation at the pit-head in many countries for this classifies the material for the market and is also a preliminary to the cleaning operation which is becoming quite common

Cleaning makes it possible to recover part of the coal which might otherwise find its way to the dumps Moreover, fine coal produced during the mining operations could be brought to the surface and cleaned and sold instead of being left underground to become a source of danger through liability to spontaneous combustion, production of coal dust, etc In countries where coal cleaning has become common, the consumer has begun to appreciate the value of a clean product Moreover the cleaned product pays freight only on the material which is usable and not on the impurities, for instance, coal with 10 per cent ash is paying freight unnecessarily on a tenth of its weight between the pit-head and the consumer's stockyard Hence coal preparation also makes for conservation

The coal, when it reaches the consumer, should be put to the best use possible. Research and experience have proved that certain coals are best suited for certain purposes In the case when coal is used as a general fuel, prevention of the loss of valuable by-products is a necessary measure of conservation Recovery of by-products will not be an economic proposition unless there is a market for them But it must be remembered that markets do not come into existence by themselves but have to be created and carefully developed As an example might be cited the case of nickel which came into prominence during the Great War, but which has now assumed enormous importance as a peace time metal through intensive research and propaganda by the producing companies It should therefore be quite possible to put on the market carbonised coal from which the greater part of the volatile materials have been extracted Various methods of carbonisation, improvements of fuel efficiency, manufacture of liquid fuels from coal, etc should therefore be studied in relation to the types of coal available in the country We are nowadays producing appreciable quantities of soft coke by the crudest of methods, completely wasting all the valuable volatile constituents The recovery of these products will be a useful measure of conservation There is much scope in India for the manufacture of motor fuel from coal, since the petroleum resources of the country are limited Countries similarly situated with regard to domestic petroleum—*e g* England, Germany and Japan—are now engaged in meeting the deficiency by using coal as the raw material for the manufacture of liquid fuel Again, with two important coalfields within easy reach of a great consuming centre like Calcutta, it should be possible to produce much of the power requirements cheaply in a few large central power stations based on coal

There is a vast field for research in Indian coal A few lakhs of rupees spent on research will result in several-fold return to the country in the shape of prevention of waste, improvement of fuel efficiency and the starting of new industries to supply many of the articles which the country is now forced to import at great cost

COAL IN RELATION TO METALLURGICAL OPERATIONS

By CYRIL S FOX, *D Sc*, *M I Min E*, *Geological Survey of India*

Although the total world output of coal averages one thousand million tons annually, only one-fifth of it is used as a raw material (15 per cent in the preparation of coke and 5 per cent in gas works) and the remainder is all used as fuel and most of this coal is burned for steam raising In India, where the coal production during 1938 was over 28 million tons, barely 2 5 million tons or about 9 per cent was used as raw material, most of it for coke making, for the smelting of iron ore and the preparation of steel

Thus by far the greater part of the coal raised in India is burned raw as a fuel In this connection I would like to say that the calorific value of Indian coals from the Damodar Valley fields averages from 13,500 B T U's per pound in the best qualities to somewhat more than 11,000 B T U's in the inferior grades, but 13,000 B T U's may be taken as a mean of the coals now being exploited In the case of the high moisture coals of the Central Provinces the average calorific value may be taken as 11,000 B T U's per pound

Physical chemists in India have complained that there is a tendency towards misunderstanding in the use of the terms B T U's per pound and calories if the latter term is not made quite clear, *i e* whether we mean kilogram-calories or calories per pound Since one kilogram equals 2·204 pounds and one degree centigrade represents 1·8 degrees fahrenheit, it is clear that one kilogram-calorie must equal 3 968 B T U's If therefore we adopt the term calorie for kilogram-calories we cannot apply it to any other measure

Now returning once more to the subject of fuel for metallurgical processes it is of interest to consider the coke in a blast furnace It is estimated that about 1·8 tons of iron ore with 1·1 tons of coke will normally yield one ton of pig iron In the process of smelting about one-third of the coke, say 7 cwts in this case, is actually involved in the reactions which result in the reduction of the highly heated iron ore to produce the iron. Here again, then, the major part of the coke, two-thirds, is consumed in heating and melting the charge in the furnace

If we examine the metallurgical processes involved in dealing with copper, lead, zinc or other ores we find very little insistence on the nature of the fuel and in fact there is a tendency in almost all these cases to adopt electrical energy for heating. In the case of aluminium there can of course be no other as the process at present employed is both electro-thermic as well as electrolytic. The great difficulties in zinc extraction, due to the necessity of using a distillation process, are being partly met by electric methods of heating. One may go on repeating various cases.

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It is when we come to questions of making ferro-alloys and special steels that the question of their preparation in this country becomes direct India and Burma have become noted for the chromite, manganese and tungsten (wolfram) ores which are almost entirely exported It is thus a question whether these important substances cannot be used for the preparation of ferro-alloys in this country, and this again brings in its train the problem of coal as a direct fuel vs electricity obtained from coal or from water-power Except in special instances, as in the case of the Mettur project, where the electric energy is a by-product water-power cannot be as attractive as coal in a coalfield's power station for the generation of electric energy

The main problem is that of cost Can we generate electric energy from coal at so low a price as to carry on the manufacture of say ferro-manganese in the Central Provinces where rich manganese ore is available but the coal is of a relatively low calorific value? If electric energy can be generated cheaply enough for the electro-metallurgy of ferro-alloys in India, can it not be used also for the electric smelting of iron ore in a modified blast furnace on the Trölhatten (Swedish) pattern? Again I must say that it is a question of cost

Theoretical calculations show that raw coal used direct will be the cheapest fuel unless the cost of the equivalent amount of coke is as cheap, and, again, whether the electric energy can be generated at a cost where the electrical power is equal to 0 66, *i e* two-thirds, of the cost of the coke These are questions of importance and of a 'fundamental character They are simple and involve principles we have to consider when examining how the conditions may be satisfied

APPENDIX I

Electrical power and energy

1. One Kilogram Calorie or *Cal* = 2·2 *Calbs*
= 3·88 B T.U's
= 1,000 gram calories or *Cals*
One Pound Calorie or *Calb.* = 453 6 " "
One B T.U. = $\frac{5}{9}$ *Calbs.* = 252 " "
One Evaporative Unit = 976 B.T.U's

2. One amp. through one ohm produces 0·238882 cals. per sec , *i e* one watt = 0·238882 cals. per sec. = 0·0568776 B T U's. per min. and one kilowatt or Kw. = 14·3329 cals. per min. One kilowatt hour = 859·974 cals. = 3412·66 B.T.U's *

3 As the year contains 8,766 hours one kilowatt continuously produced for a year yields 29,895,902 or say 30 million B.T U's which is somewhat less than that yielded by one ton of good coal averaging 14,000 B T U's. per lb. which equals 31 million B.T.U's and since one E H.P. year is 22,320,000 B.T.U's the heat value of coal is 1⅓ E.H.P. year also one lb. of coal produces as much heat as 4 Kw. hours. (See above *.)

4 Thus when a consumer pays 2 annas per unit for electric energy (light) where coal costs Rs 8 per ton, the ratio of the electrical heat Rs 0-2-0 × 8766 × 1⅓ = *Rs 1,461* to Rs 8 the coal heat is as 180 to 1 And in a generating station where the unit is one pice and coal is Rs 2-8-0 the ratio will be over 200 to 1 and cheaper units should be possible

5 Efficiencies of furnaces for melting metals .—

Coke-fired crucible steel furnace	2 to 3 per cent
Reverberatory furnaces	10 to 15 ,,
Regenerative open hearth (steel)	20 to 30 ,,
Shaft furnaces (cupolas, etc)	30 to 50 ,,
Large electrical furnaces	60 to 85 ,,

It is thought that similar efficiencies would be obtained for the same furnaces if employed for smelting ores

(' The Electric Furnace ' (1914) by Alfred Stansfield, 2nd Edn , p 40)

APPENDIX II

Melting temperatures of metals and heat required

Metal	C°	F°	*Calb*	B T U	Watt hours
Tin	232	450	28	51	15
Lead	327	620	16	28	8
Zinc	419	786	68	122	36
Aluminium	657	1214	256	465	136
Brass (65 Cu)	920	1688	130	234	60
Copper	1083	1983	162	292	85
Cast Iron	1200	2192	245	441	129
Tool Steel	1425	2600	300	540	158
Wrought Iron	1500	2737	343	617	181

COAL IN RELATION TO POWER

By CYRIL S FOX, *D Sc , M I Min E , Geological Survey of India*

It is unnecessary to discuss questions of power from the sun's heat, the tides, or the wind, as these are not serious considerations at present when we can secure relatively cheap power by well-known methods from hydro-electric sites, fuel oil and coal It is to these I will draw attention

Water-power has come to be understood as one of the cheapest means of supply because the cost at Niagara Falls, Kinlockleven (Scotland), and in Norway and Sweden are said to average, respectively, Rs 60, Rs 28 and Rs 16 per kilowatt year or from 0 10 to 0 03 annas per unit (kilowatt hour)

This kind of cheap power may be available in this country when the discharge water is saleable for irrigation purposes and the storage dam a part of an irrigation scheme This is the case at the Mettur project in Madras which is also close to a railway and to deposits of magnetite and magnesite for the possible preparation of electrically smelted special steels and metallic magnesium

With regard to oil fuel the demand may be gauged by imports of nearly £2,000,000 from Iran, while the imports of Burmese petrol (£2,000,000) and kerosene oil (£4,500,000) are still higher These are all costly items and as India produces only about 75 million gallons of petroleum (£1,000,000) the threat of imported oil fuel for power purposes can be discouraged by attending to the subject of liquid fuel by-products from Indian coal.

In 1938 the Indian production of coal was over 28 million tons valued at Rs 1,064 lakhs (£8,000,000) and of this total perhaps one-ninth was used as raw material in making hard coke or in manufacturing gas The remainder was burnt raw as fuel, largely for steam raising for power purposes in various industries, on the railways and for ships And most of this coal, which was used as fuel, was burnt as raw coal

If we consider that, say, 21 million tons of coal were burnt raw, we also conjecture a vast loss of rich gases, upwards of 200 millions of gallons of valuable tars (saleable at £2,500,000—Rs 330 lakhs) and other by-products However much we may at present deplore this, we must face the actual facts of the case, and these are that the raw coal is cheap and may be burned with great thermal efficiency in boilers.

The average pit mouth's value of Indian coal in the chief producing area of India—the Damodar Valley—is probably Rs 2-12-0 and might sometimes be reduced to Rs.2 in many cases The calorific value of these coals vary from over 13,000 B.Th.U's. per lb to 11,000 B.Th U's. and the average can be taken as about 12,000 B.Th U's. This represents nearly 27 million B Th U's.

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per ton so that roughly 2·5 tons of coal can yield 2 kilowatt years of electrical power (3 electrical horse power years)

Turning now to the generation of electrical power in practice we have to allow for losses in transfer of heat through mechanical energy to electrical power which, in an overall system of boilers-turbo-generators, may not exceed 15 per cent. So that roughly 8 34 tons of coal are required per kilowatt year. Presuming the generating station was at or near the colliery and the coal cost Rs 2-8-0 per ton, the cost per kilowatt year would be Rs 21 or 0·038 annas per unit (*i e* per kilowatt hour)

Estimating for a 100,000 kilowatt station operating at full load or at least a high power factor we may allow Rs 250 per kilowatt for the cost of the plant (machinery, etc) or a total of Rs 250 lakhs which at so high an interest at 4 per cent would add Rs 10 per kilowatt year to the price of power Alluding next for working expenses, upkeep, transmission and profit—say Rs 29 per kilowatt year, we get a total, rather optimistic perhaps, figure of Rs 60 per kilowatt year or 0·112 annas per unit (1 4 pies) which is the same as the average for Niagara

It is not to be forgotten that I have estimated generously for coal which can be got more cheaply and also for interest on capital, but I have not faced the full question of power factor and some of you may consider that I have overlooked such important details as water supply for the cooling system which may require 6 to 10 million gallons a day I have found several sites in the coalfields, both for cheap coal and sufficient water, and venture to say that cheap power from coal could be secured at about the cost I have estimated if it can be all sold

I must again return to the subject of burning raw coal as against recovering the by-products, and I venture to lay down a general principle This is that the by-product recovery will only lower the power cost where the power station is actually in a great industrial works, but in separate isolated power stations it is better to use raw coal in pulverised form of suitable, though not necessarily of the best, quality Much of the ease of working will depend on the character and amount of the coal ash If the coal has a high ash content but the ash is of low fusibility it will readily form slag which will be easy to handle and dispose of.

CARBONISATION OF COAL AND RECOVERY OF BY-PRODUCTS

By B WILSON HAIGH, *M L.A. (Bihar), M I Chem E*

No excuse is needed for the inclusion of this subject in the symposium 'Coal in India', for the subject is one of tremendous importance in the industrial life of the country and especially the Province of Bihar

What is meant by Carbonisation

When coal is heated in the absence of air so as to expel part or nearly the whole of the original volatile matter of the coal, it is decomposed and the process is termed destructive distillation With coking coals, however, the particles fuse together, coalescing to form a coherent mass which is called coke The carbon residuum of the original coal has become cemented with a binding ingredient formed or liberated during the heating Coals with a high binding power are called strongly coking coals, those with a low binding power are feebly coking; there are also non-coking coals which have no binding power at all such as anthracite When the coal is heated to temperatures varying from about 400°–700°C. the operation is generally known as Low Temperature Carbonisation When the temperature to which the coal is subjected is between say 900° and 1300°C this is called High Temperature Carbonisation and this is the one which is practised in India There is also Medium Temperature Carbonisation carried on at a temperature of about 800°C, little practised as yet but about which more will be said later If non-coking coals are so heated as to drive off most of the volatile matter and afterwards allowed to cool, the residue appears to have the same form as the original coal, so that if the coal is first crushed, nothing but a black powder remains after heating.

High Temperature Carbonisation.

This may be conducted in beehive ovens which are firebrick chambers shaped like a beehive The heat retained in the structure commences the distillation, the gases given off from the coal mix with air which is allowed to enter above the door and combustion takes place—the heat reflected from the dome carries on the carbonisation—the products of combustion pass out at the top of the oven Very good coke can be produced in this way and also in the 'Country oven' which is a long narrow rectangular chamber where the heat is also produced by the combustion of the evolved gases. This process is slow, the carbonising time varying from say 48–72 hours but nowadays furnace and foundry cokes are chiefly made in the by-product oven.

This is the source of most of the coke used in the iron and steel industries today. In the beehive oven process the only product is coke but, as is implied

[Published August 19th, 1940

in the name, the by-product oven is the source of by-products—coal gas, coal tar, ammonia, benzole, naphthalene and some others

Some idea of the magnitude of the coking industry may be gained from the Report of the Chief Inspector of Mines in India for year ending December 31st, 1937 He gives the figure of 1,848,521 tons coal despatched from Jharia alone to coke factories and 88,540 tons of hard coke despatched from Jharia 786,126 tons of soft coke were also despatched from Jharia, mostly made, not in ovens, but by the 'heap' method There are vast deposits of first class iron ore in Bihar The best coking coals are also mined in Bihar so that with one exception the large coke factories are situated at the collieries in Bihar or the Steel Works of Tatas' also in that province The iron ore is so pure that coke of a higher ash content than is generally used in steel manufacture in other countries can be used in India The lowest ash in Indian-made coke is about 15% and it is often used up to 22 or 23%, and even then sometimes less than 18 cwts of coke per ton of pig iron is used in the blast furnaces

The by-product coking industry is of comparatively recent growth, the first by-product coking plant in Great Britain was installed in 1881 by Henry Simon working in conjunction with Francois Carves, a distinguished French engineer, and the first plant in India was built by the same firm (Simon-Carves, Ltd) at Giridh in 1909. Since then enormous strides have been made and in 1940 it is anticipated that at Tatas' Works in Jamshedpur they will be able to manufacture over 3,500 tons of coke per day or 1,300,000 tons per annum This plant will be the largest single coking plant in the British Empire with a maximum capacity of 5,400 tons of coal per day

Described in non-technical language a coke oven is a long rectangular chamber built of firebrick, or silica bricks Ten metres (33 feet) used to be the standard length with a height of 2½ metres, but the modern tendency is to build larger ovens and the latest type in India measure 44 feet 5 inches long by 14 feet 7 inches high by 17½ inches mean width These ovens each take a charge of 20 tons of coal and are capable of carbonising this in 15 hours, the normal operating time is 18 hours On either side of the chamber are flues heated by gas and underneath is a sole flue similarly heated. The gas used for heating is generally that produced in the process which is normal coal gas. Its composition varies The following figures are typical:—

	Per cent.
Carbon dioxide	0·7– 2·0
Benzol, etc.	0·6– 1·5
Heavy Hydrocarbons and Tar	1·0– 5·0
Carbon Monoxide	5·0–10·0
Methane	24·0–36·0
Hydrogen	50·0–59·0
Nitrogen	1·0– 6·0
Hydrogen Sulphide	0·1– 1·0

The quantity of gas evolved from 1 ton of coal varies of course but an average figure is 10,000 cu ft per ton having a heating value of 450–500 British Thermal Units (net) per cubic foot This is called 'rich gas' and is a very valuable heating agent Sometimes all the coke oven gas is used for heating purposes as at a steel works or it may be sold for domestic lighting and heating in cities or towns

In that case the ovens have to be heated by 'lean gas' either blast furnace or producer gas and under those circumstances a special type of oven is available called the Compound Oven These are of course of the regenerative type where the air for combustion is strongly pre-heated The products of combustion are passed through a chequer work of firebrick which becomes heated to a red heat and after half an hour, air for combustion is passed through the regenerator. There are two sets of these and they are used alternately every half hour During one period they are heated by the products of combustion and during the other period air is passed through to be heated Where 'lean' gas is used the gas is also pre-heated in a similar way before combustion through a separate regenerator

The coal is charged into an oven through suitable openings in the top, the charge is levelled by a long arm operated electrically passing over the charge and the doors and charge holes are made gas-tight

The leveller is attached to the ram or coke pushing machine which discharges the coke into a car in which it is quenched by water or on to a coke bench of cast iron plates where it is cooled in the same way The products of distillation escape through the ascension pipe controlled by a valve into a collecting main which is constantly flushed either by tar or liquor to remove the dust which is carried in the gas stream

The gas is pulled away from the collecting main by means of an exhauster and forced through the different pieces of apparatus where the by-products are removed, back to the return main where it is burnt in the heating flues or supplied for other uses In the most modern types of ovens as much as 60% of the gas may be 'spare' and available for uses other than heating the ovens The cycle is continuous and there is rarely any gas-holder provided for gas storage and when for any reason the cycle has to be interrupted the whole of the gas has to be by-passed and the crude gas blown away into the air—an operation in which there is an element of danger and which needs great care

Oven Construction

Nowadays ovens are built on a reinforced concrete decking supported by reinforced columns carried on a reinforced concrete raft This is necessary owing to the larger modern ovens being so much heavier. Brickwork arches which were formerly used could not support the great weight of the modern superstructure.

In the construction of the ovens refractory material of the highest grade has to be used and it is a fortunate circumstance that there are ample supplies of first class fireclay and silica materials within easy reach of where they are required The manufacture of refractories has progressed in Bengal and Bihar to a remarkable degree It is now acknowledged that the special shapes in fireclay, semi-silica and silica which are required in coke oven construction can be manufactured of as fine a quality, with as great precision and with as small a tolerance as in any other country

It must never be forgotten that the most important product from coke ovens is coke and it is the duty of the coke works manager to produce the best possible product from the coal at his disposal If he uses different coals careful blending is called for and a variation in the coking time may often make considerable difference to the resultant coke

If the blast furnace manager is to get the best results, what he aims at is to reduce coke consumption to the minimum so as to get the lowest coke consumption per ton of pig iron. To do this he must have coke of regular quality, sufficiently hard to stand the burden of the furnace (that is why soft spongy coke is useless for the purpose) On the other hand it must not be too hard or lacking in porosity otherwise it would pass down the furnace into the slag at the bottom without performing its function, which is to reduce the oxides of iron to the metallic state That is why the 'Jhama Coke', a natural coke produced by the carbonisation of certain Jharia coal seams *in situ* is useless for blast furnace work It is so hard and non-porous because it has been coked under such great compression of the overlying strata Coke is also used in foundries for melting iron and brass to make castings It is used in sugar factories, aerating gas factories for producing CO_2 and in smithies for blacksmiths' use

Coke also contains sulphur and phosphorus and a portion of these finds their way into the pig iron during the blast furnace operations, when in excess both have a deleterious effect on the pig iron Fortunately Jharia coals are very low in sulphur—the best contain only about 0·5% which is negligible Giridih coke is particularly low in phosphorus and so is suitable for the manufacture of ferro-manganese

Nothing has been written about gasworks practice which is also a branch of high temperature carbonisation This is conducted in nests of fireclay retorts and the chief product is not coke but illuminating gas and the retorts are heated by burning coke, the balance being sold as gas coke for domestic use

Tar and ammonia are also recovered and the gas is stored in large gas-holders and distributed through a system of mains and metered to the various consumers for commercial or domestic heating, cooking and lighting As is well known, some Calcutta streets are lighted by coal gas

Low Temperature Carbonisation.

In this system the coking temperatures range from about 550° to 700°C or a little higher The main objects of thus restricting the temperatures are·

(1) to obtain maximum yields of liquid products, and (2) to produce free burning semi-cokes containing proportions of volatile matter ranging from 8% up to about 20% The yield of rich gas in L T systems will range from 2,000 to 7,000 cu ft per ton of coal and its calorific value may be from 700 to 1,000 B Th U's per cubic foot

Generally speaking, the gas and oils from the L T process are mostly of the paraffin series of hydrocarbons whilst high temperature carbonisation yields aromatic hydrocarbons of the benzene series

The chief product of the Low Temperature process is a smokeless fuel and several successful fuels have been marketed in England, notably Coalite, but it can only be regarded as a luxury fuel for it is sold at a high price somewhere round 45 shillings per ton, higher than that of best house coal A vast number of experiments have been done during the last 30 years, many systems have been tried on a semi-commercial and commercial scale, hundreds of patents have been taken out, millions of pounds of capital have been expended most of which has yielded no return to shareholders, and where profit has been made it has only been due to the 'fancy' price which the producers have been able to obtain for their smokeless fuel The main fillip to this industry comes from the patriotic people who deplore the smoky atmosphere of England's cities and towns and who try to do their bit to reduce it and the resultant fogs, by burning a smokeless fuel

The British Government have tried to help by grants-in-aid and by purchase of the Low Temperature oils for use in the Navy but even with these adventitious aids the prospects are not favourable

There is much loose talk and often ill-informed newspaper correspondence in Calcutta and elsewhere asking why large-scale Low Temperature plants are not established in the coalfields to recover the valuable by-products (dyes, etc) which are now being lost The Bihar Government are making experiments with this system but they are instigated by those who have a rather limited knowledge of the subject and are, in the opinion of the writer, likely to meet with little success

The capital cost of such plants is high Where is the profit to come from to pay the interest,—after providing for the overhead charges and working costs,—let alone any dividend ? Where is the market for the semi-coke at a price that will pay ?

Other products are Low Temperature tar of which 10–18 gallons may be recovered from a ton of coal but as it is not suitable for road tar, where is the market for it ?

Sulphate of ammonia is also recoverable but probably not at a profit Sulphuric acid has to be manufactured or bought and some coke plants have already ceased to recover this by-product as it cannot compete with synthetic ammonia Motor spirit is another recoverable by-product but has to pay an excise duty of 10as. per gallon (now 12as). Even on a large scale it would cost 4 or 5 times as much to manufacture as petrol, so again how could it be sold to compete with petrol and yield a profit? These facts should be known before Governments or investors sink money in projects which under present conditions have little hope of success There are many difficulties in the way, both technical and other, and probably no other technical process has yielded so many disappointments

Medium Temperature Carbonisation

This is a process which lies in between the high and low and may be conducted at temperatures round about 800°C

Its main object is the production of a smokeless domestic fuel

There are now more coke plants in India than are required to produce the hard coke required for the iron and steel industries and coke oven owners may now be compelled to turn their attention to the domestic coke market

The adaptation of coke ovens for the production of a free burning reactive coke has been proved to be possible notably in France and less in Great Britain and the time is soon coming when close attention will have to be given to the subject in Bihar Soft coke as made in heaps or mounds is sold very cheaply as there is no capital expenditure involved in its manufacture but generally speaking it is a very low grade fuel though the Soft Coke Cess Committee are trying to improve it and push its sale which is increasing fairly rapidly (786,126 tons were sold in 1937 and over 900,000 tons in 1938)

If, however, a demand for a clean readily ignitable fuel at a higher price than soft coke can be created and developed there must be a great potential market in India No doubt the difficulties are many, a very highly developed marketing organisation would need to be established and the fuel would probably have to be delivered in jute bags by lorry from house to house on a cash basis.

It may develop into a profitable distributing agency if properly organised and managed

The by-products produced at 800°C are of a character similar to those obtained in normal high temperature carbonisation and are thus more valuable than the paraffinic bodies obtained by carbonisation at low temperatures.

CARBONISATION OF COAL

By W. J Savage,[1] *A M I Chem E*

The history of carbonisation of coal goes back about two hundred and fifty years but progress was slow until a hundred and fifty years ago when William Murdoch first used gas for public lighting From that time a great industry has developed and gas supply is one of the most important public utility undertakings in modern life

Until recent years the carbonisation of coal was considered as 'destructive distillation' but with the increased importance of the by-products—coke, tar, etc —this phrase is falling out of use During the past two decades a large amount of scientific work has been carried out to determine the best conditions and type of plant employed

It is generally accepted that coal is the product of the decomposition, under great pressure, of vegetable matter During this process, the carbon content increases and the hydrogen and oxygen contents decrease The percentage of volatile matter decreases until at the stage when the hardest coal, anthracite, is formed, the proportion is only about one-sixth as compared with that of lignite, which may be considered as a midway product in the formation of anthracite from the original vegetable matter

The question of finding the most suitable coal is of vital importance to the Gas Engineer and is influenced by several factors These factors also determine the kind of plant in which the carbonisation is to be carried out Practically all coal is carbonised in one of the following types of plant :—

(1) Horizontal Retorts.
(2) Vertical Retorts
(3) Coke Ovens.
(4) Chamber Ovens.

If the main product required is Town Gas, either of the first two is generally used. If hard coke for metallurgical work is the main product, coal is carbonised in the third type of plant The fourth system, Chamber Ovens, is a combination of the two. In addition to these types there is another system coming into use for the production of light oils, benzols, etc., by the carbonisation of coal at low temperature but the amount of coal so carbonised is very small at present.

Horizontal retorts are usually made of fireclay and the dimensions are 20 feet × 22 inches × 16 inches, the section being a rough ∩ shape. The general practice is for the retorts to be set in a 'bed' of four tiers of two retorts

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[1] The Oriental Gas Co., Ltd., Calcutta.

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At each end of the retort a cast iron mouthpiece is fitted from which the gas as generated is carried off through iron pipes to a hydraulic main fixed on top of the bed The pipe from the mouthpiece is sealed, usually about ½″, in liquor in the hydraulic main The mouthpieces are fitted with doors which are hermetically sealed by means of an eccentric lever When the doors are opened for charging with coal or pushing out coke the seal prevents air being drawn in and mixing with the gas The 'beds' are heated by producer gas generated from coke and each bed is a separate unit with its own furnace The temperature of carbonisation reached is 1250°C When a retort is emptied of coke produced from the previous charge of coal another charge is put in by means of the stoking machine and the doors are closed as quickly as possible With Indian coal the average weight of the charge is 10½ cwts and the period of carbonisation is 10-11 hours By the end of that period all the gas is driven off together with all tar vapour, etc and only coke remains The gas, tar vapours, etc are drawn through the condensing plant, where the tar condenses out, by means of 'exhausters', and then passed through the washing and scrubbing plant to remove cyanide products and ammonia and finally through large cast iron chambers (purifiers) containing ferrous oxide to remove sulphuretted hydrogen

In vertical retorts the coal gravitates through the retorts and the residual coke is extracted at the bottom In the majority of vertical retort installations the process is continuous although there are a few where the charge of coal is dropped in and left until the carbonisation is completed when the coke is released into wagons by opening the bottom door In the continuous process, coal enters at the top and coke extracted from the bottom This process ensures a regular quality of gas produced The heating of the retorts is by producer gas and usually is so regulated that the top 5 or 6 feet of the retort is comparatively cool, the centre section is heated to a temperature of 1300°C and the bottom section of the usual 25 feet length of retort is progressively cooler than the middle section Near the bottom a controlled supply of steam is admitted which, meeting the incandescent coke, combines with the carbon forming 'water gas', which may increase the yield per ton of coal by 30%, this latter figure depending, of course, upon the quality of gas required A further effect of admitting steam is that the water gas scours the plastic coal and washes out many gaseous hydrocarbons which otherwise would be decomposed if left in contact with the hot sides of the retorts

In India the bituminous coals used for gas manufacture are not of a very wide choice All coals, of course, will produce gas but the most suitable are of a limited quantity in this country. A Gas Engineer firstly requires a coal that will give a large volume of gas after purification but also he must have a coal which will produce a good saleable coke and a fair yield of tar The moisture content of the coal should be very low because when coal is brought into the retorts the first substances to be distilled are the free water and light oils. If the water content is high, too much weak virgin ammoniacal liquor is produced which reduces the efficiency or increases the cost of the production of ammonium sulphate

A proximate analysis of good gas coal in India is—

Moisture	1·5%	
Ash	11·0%	dry basis
Volatile Matter	34·5%	
Fixed Carbon	54·5%	

with the calorific value over 13,000 B Th Us per lb

The ash content is at least twice as high as that of good English gas coals and the fusion point of the ash is low This latter factor has a bad effect upon the producers which supply the beds with gas for heating and it is necessary to adopt special grates to prevent heavy clinker forming Also, the quantity and quality of the ash renders its use almost impossible in carburetted water-gas plants, which are frequently used in Europe as auxiliary to coal gas plants and exclusively used in some parts of the U S A and Canada

Another unfortunate feature of a good Indian gas coal is that in most cases when it is plastic during carbonisation the mass swells considerably This has in the past prevented the installation of vertical retort plants in India and has led to the loss of export trade to gas undertakings on the China coast. Two years ago, however, the Hongkong Gas Company working with the contractors who erected their vertical plant solved the problem of Indian coal 'sticking' in the vertical retorts and now have recommenced importing The Shanghai Gas Company also find they can now use Indian coal and, as supplies of Japanese coal are no longer available, may use it in preference to Australian coal which, although easier to carbonise, is dearer to purchase

One obnoxious impurity, sulphuretted hydrogen, to be found in crude gas is produced from pyrites in coal and in this respect Indian gas coals are superior in most respects to European coals The 'free pyrites' is usually well below 0·5% and the percentage of H_2S in crude gas is below 1% This small proportion is easily extracted The small amount of pyrites present reduces the danger of spontaneous combustion when stored At my works Indian gas coal is stored under cover to a depth of 15 feet and no case of fire has occurred

In carbonisation the 'decomposition point' of coal varies with different kinds of coal. When coal is first heated in a closed retort or chamber occluded gases are first given off These gases are mainly paraffin hydrocarbons and are given off at temperatures between 150–200°C Water vapour and light condensable oils are given off up to about 400°C and during this range sulphur compounds and oxides of carbon are evolved. From 400°C large volumes of gas which are rich in hydrocarbons are produced. These hydrocarbons combine with the lighter oils, benzene, toluene, etc and form 'gas tar' Above 1000°C only gas containing a large percentage of hydrogen is evolved The original nitrogen in the coal, plus some of which may have leaked in during the process, combines with the hydrogen and forms ammonia It can be assumed that the maximum combination occurs when the retort is at a temperature of about 1000°C, and if the carbonisation of coal is carried to the extreme, say several hours at 1300°C, the total quantity of ammonia produced is not greatly increased If the gas is not extracted from the retorts, the ammonia would be decomposed before the retort reached 1000°C and it has to be remembered that during carbonisation, when the temperature is rising to say 1250°C, the gases evolved are being continuously extracted by the exhauster There is no doubt the presence of other gases prevents or retards the decomposition of ammonia Some of the original nitrogen in the coal combines with the hydrogen and the carbon of the incandescent coke to form hydrocyanic acid and also a little free cyanogen HCN does not form below 900° and it is believed that at the higher temperatures some of the ammonia is decomposed by the incandescent coke to produce this impurity which has to be removed

The proportion of carbon dioxide in the gas produced would be about 1% if the coal were distilled in a hermetically sealed chamber In practice such conditions cannot prevail and air and waste gases from the exterior of the retorts enter through the pores or cracks in the fireclay retorts, the interior of the retort being kept at about 2/10ths of an inch vacuum The oxygen so entering combines with carbon of the incandescent coke or gaseous compounds and carbon dioxide is formed It is the aim of a Gas Engineer to keep the percentage of this 'inert' constituent of the gas as low as possible

Where coal gas is supplied to consumers the quality is governed in most countries by Acts and the undertaking is severely penalised if the calorific value falls below the standard defined or if sulphuretted hydrogen is present The general standard for the United Kingdom is 450 B Th Us per cubic foot of gas The problem that has to be met is to obtain the highest yield of gas per ton of coal whilst keeping the quality of the gas supplied above the standard calorific value All good gas coals if distilled in a perfect atmosphere in the retort, that is the gas is extracted as generated without either pressure or vacuum, would produce gas at the temperatures prevailing too rich with a corresponding low volume In horizontal retorts the gas during the first three hours of carbonisation would contain such a high percentage of hydrocarbons that the usual burners of consumers' appliances could not supply sufficient air for combustion and long smoky luminous flames would result. On the other hand the gas produced during the last three hours of carbonisation would be of low calorific value as the hydrogen proportion rapidly increases. To obtain a satisfactory mean and to produce a gas of consistent quality the charging of retorts is spread over the period of carbonisation. In India where the retorts are set in four tiers it is the practice to 'charge' the retorts of each tier in turn spreading the whole operation to cover the 10-11 hours of carbonisation. This means that gas generated in each 'bed' is being generated from coal in four different stages of carbonisation with the result that the gas is well mixed before passing through the condensers, washing plant, etc to the holders for distribution to the town To avoid waste through the porous retort material it is usual to keep a slight vacuum—about $\frac{2}{10}$ inch water gauge—inside the retorts This is controlled by a water-sealed governor fixed on the foul main between the hydraulic mains and the condensing plant Should any variation in the quality of gas produced as indicated by the recording calorimeters occur the attendant can immediately restore conditions to normal by altering the 'pull' on the retorts by adjusting this governor If the calorific value of the gas is too high a little extra vacuum will remedy this and *vice versa*

In both systems of carbonisation—horizontal and vertical retorts—the most economical working is obtained by removing the hydrocarbons away from the incandescent coke or sides of the hot retorts before decomposition (or degradation) has proceeded too far It is a matter of experience to determine with each installation and each coal or blending of coal which conditions give the best results The decomposition of the hydrocarbons lowers the quality of the gas and also adversely affects the tar When the decomposition occurs some of the liberated carbon is carried forward by the gas and deposits in the condensed tar increasing the percentage of 'free carbon'

It is not possible to say which system of carbonisation is best as every installation has to be considered in relation to local demand for gas and type of coke and also the kind and cost of coal available for carbonisation.

FUEL OIL FROM INFERIOR JHARIA COALS

By S K Roy, *Ph D (Zurich), Dhanbad, and* S S Ghosh, *M Sc , Patna*

The existing coke ovens, owned by the Government and big industrialists, utilise superior grade coals for making hard coke and many of them also recover the various by-products of this high temperature process So we already possess, thanks to the well-equipped coke ovens at Giridih, Bararee, Jamshedpur, Burnpur, Kulti, etc , a substantial knowledge of the gas and tar contents and in some cases of other products of the superior class coals of the Jharia Coalfield which is now mostly used as fuel S S Ghosh, H K Sen, Dr Sanjana, Dr Bhattacharjee, Dr Mukherjee, Dr Ghosh and others have also interested themselves from time to time with the low temperature carbonisation of Indian coals, but in most cases they interested themselves only with the 'aristocrats' of our coals, and sometimes the samples treated were rather indefinite and unspecified. But whatever may be the case with our high grade coals nothing so far is known about the gas and tar-producing capacities of the immense quantity of second class coals used in the Jharia Coalfield for making soft coke nor do we know anything about the composition of the gas and the derivatives of the tar they produce, although in the manufacture of soft coke about one-third of the coal is lost in the form of gas and tar

So far as we know, only Dr C Forrester, Principal, Indian School of Mines, has carried out in a systematic manner the distillation tests of this type of second class coal utilised for soft coke making, and has determined the tar contents of the coals under various temperatures But he too has not fractionated his tars and all his results are the property of the Soft Coke Research Committee who have not yet published them.

Taking the most conservative estimate of about 2 million tons of soft coke being annually manufactured in the Jharia Coalfield for which 3 million tons of second class coal is burnt, and putting its tar content at the moderate figure of 10 gallons per ton of coal used, about 30 million gallons of tar, comparatively rich in motor spirit, light oils and other substances, are lost to our country per year. It is, for this reason, that we undertook firstly a series of researches on the gas and tar contents of the poorer grade coals used for soft coke making in the Jharia Coalfield and subsequently endeavoured to find out what are the by-products of this tar. The results of our experiments are given in the following pages The experimental work was carried out by the junior author in the laboratories of Prof. B. C. Roy, Science College, Calcutta University, under the direction of the senior author and with financial assistance from the senior author and his colleague Prof. S. K. Bose.

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Experimental details

The experiments were carried out in a cylindrical mild steel retort prepared out of a piece of steam pipe of 5″ inside diameter and 2′-9″ long The thickness of the wall is ¼″ During the first two experiments the pipe was closed at one end with a screw cap while the other end was provided with a reducing socket 5″ to 1″ connected with a 1-inch elbow pipe for the extraction of volatile matter This is more or less similar to the arrangements made on a previous occasion for experiments similar to the present ones by the junior author jointly with Dr H K Sen (S S Ghosh and H K Sen—*Proc Inst Chem India*, Vol VI, Part 2, 1934)

But difficulties were experienced in the discharge of coke from such a retort and after the second experiment we were obliged to think out a more suitable retort for further experiments The reverberatory furnace employed on a previous occasion (*loc cit*) for similar experiments was not found suitable on actual tests as it could not maintain the necessary temperature of 500°–530° Centigrade required for our experiments On account of its firing arrangements from below it used to get very hot in the lower parts—the temperature rising there in the neighbourhood of 750° Centigrade—but in the upper part it was difficult to maintain constantly even 500°C In order to eliminate this difficulty, we decided, after some discussion, to change the vertical retort into a horizontal one with the following special arrangements for maintaining uniform temperature throughout the retort Most of the laboratories engaged in low temperature carbonisation work never recommend vertical retort systems, though in large-scale commercial works both types of retorts are in vogue.

The following is the description of our retort and firing system —

Two flange-heads were welded at two ends of the retort, front and back, and they were provided with removable caps fastened by nuts and bolts. Then, instead of heating the retort from one end, arrangements were made to heat it over its full length by putting it in a horizontal position. And, instead of heating it by direct flame, in which case the portion in direct contact with the flame may be hotter than that in the upper part of the retort, the retort was placed inside a 'tunnel furnace' made of fire-bricks. A space of about 1″ was left all round the retort between the tunnel furnace and the retort-wall for proper circulation of hot air from below and equal heating all over. At about 3″ from the further end of the retort a ½″ steel pipe was welded at the side of the retort for the extraction of volatile matter generated inside the retort. The heating was done by a burner made of 1″ galvanised pipe bored at every half-inch When kindled, each hole became a burner and we had altogether about 50 burners. This burner pipe was so placed that our retort may be at a distance of 2″ from the tips of the flames. Hot air from the flame circulated all round the retort and escaped through the chimney above,

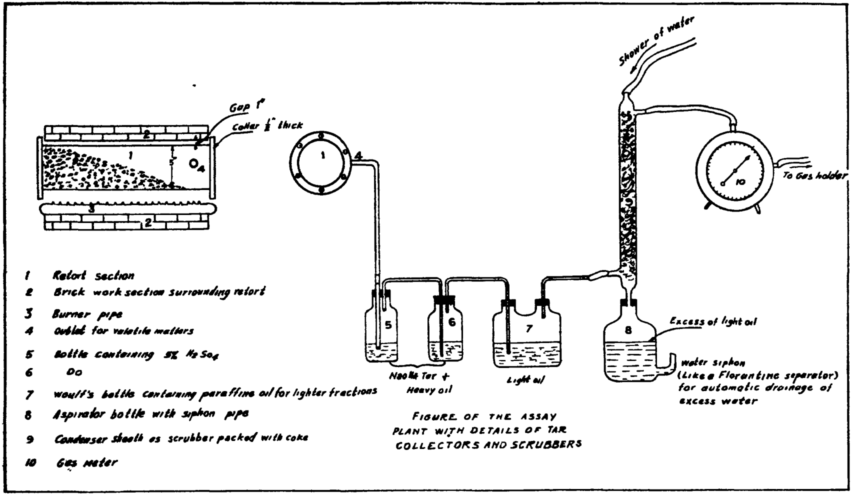
Gap 1"
Collar ½" thick
1
2
2
3
4
5"
1
4
5
6
7
8
10
Shower of water
To Gas holder
Excess of light oil
water siphon
(Like a Florentine separator)
for automatic drainage of
excess water
Naolle Tar +
Heavy oil
Light oil
1 Retort section
2 Brick work section surrounding retort
3 Burner pipe
4 Outlet for volatile matters
5 Bottle containing 5% H_2SO_4
6 Do
7 Woulf's bottle containing paraffine oil for lighter fractions
8 Aspirator bottle with siphon pipe
9 Condenser sheath as scrubber packed with coke
10 Gas meter

FIGURE OF THE ASSAY PLANT WITH DETAILS OF TAR COLLECTORS AND SCRUBBERS

FIG 1.

which was 4′ high. The advantages of this horizontal retort were found to be the following —

1 Better and more uniform distribution of heat throughout the coal mass This advantage was never obtained in vertical retorts
2 Prevention of cracking, to a great extent, of the primary products of distillation
3 Elimination of the difficulty regarding the extraction of coke experienced in the previous furnace where, in order to extract the coke, the heavy retort had to be taken out every time But in the present case coke could be extracted by pushing it out, without removing the retort from the furnace

5 to 10 lbs of coal was crushed in a jaw crusher and placed in the furnace by un-screwing the cap of the flange at the back The size of particles was ¼″ and below The flange caps at both ends were tightly fixed with bolts and nuts and asbestos packing The furnace was then connected with receivers (see figure) to collect gas, ammonia and other substances and after this was done the burners were lighted The temperature was maintained between 520° and 550° Centigrade, and this was noted by two platinum-iridium-pyrometers inserted through holes in the brick-work, at right angles to the retort The pyrometer tip just touched the retort

When we had treated a few charges we found that the conduction of heat to the centre of the coal mass inside the retort from the periphery was not quite what could be expected In some of the samples of coke we saw that although the distillation was continued for what we considered was the necessary length of time, the coking was not complete In some cases the experiment has been discontinued by us just when coking of the central portion had started, but not completed

Coal is a bad conductor of heat As soon as it is sufficiently heated, it becomes plastic along the periphery of the retort and being spongy and in continuation with a layer of semi-coke inside the retort, it becomes a still worse conductor Hence it becomes still more difficult for the heat to travel from the periphery to the core of the retort Speaking theoretically, the time 'C' necessary for complete carbonisation of a layer of coal and the thickness 'T' of the coal layer are related to each other according to the following formula —

$$C = K(T+K)^2$$

where 'K' is a constant depending on the nature of the particular coal From Allison's curves it can be easily understood by extrapolation that a bed of coal 2 to 3 inches in thickness can be penetrated by heat within 4 to 5 hours. In the retort used by us for our low temperature assay, the same thickness has been selected, and for complete coking, instead of 4 to 5 hours as suggested by Allison, we had to continue the heating for 5 to 6 hours, in each case, from the time of the first evolution of gas. The hot vapours of tar and gases, as they came out of the retort, passed through a series of collecting bottles containing absorbers, as shown in the figure A 5 per cent solution of sulphuric acid was used in the first two bottles to ensure complete absorption of ammonia and separation of tar and heavy oil, whilst the third one which was a Wolf's bottle contained paraffin oil or creosote to absorb the lighter fractions which may escape condensation in the first two bottles All these bottles were cooled by dipping them in water Next came a scrubber fitted upright on a small aspirator bottle The scrubber was provided with an outer sheath of Liebig's condenser packed with coke, over which was a sprayer spraying water all the time The water scrubbed out all the escaping gases and collected them in the aspirator bottle underneath The light oil floats on the water The excess of water runs out constantly through the syphon bend at the side of the aspirator bottle The washed gases pass through the gasometer and collect in the gas-holder After the distillation is over the contents of the first two bottles containing ammonium sulphate and tar were separated by means of a separating funnel The total liquid is made up to a standard volume and the total ammonia is determined by absorption The total tar oil separated from the liquor was treated with 5 per cent caustic soda to separate the phenolic constituents From a determination of the volume of the total tar after treatment with alkali, the percentage of phenols present in the original crude tar (sp gr 1 06) is known The neutral tar was then washed three times in water and distilled to obtain the various fractions

As it is impossible to separate the tar completely from water, and as the moist tar begins to froth as soon as it is heated, a good deal of inconvenience was experienced in the beginning to distil the tar We, however, got over this difficulty by adopting the principle of 'drop distillation', i e pouring the tar from a separating funnel drop by drop on the bottom of the distillation flask which already contained a little hot tar and a few pieces of pumice stone, also hot As each drop of moist tar came in contact with the hot tarry surface of the pumice, it distilled almost immediately without any considerable increase in volume Frothing was practically eliminated in this way If this experiment is carefully manipulated, this distillation process more or less becomes a type of steam distillation In this steam distillation at a low temperature, the lighter fractions of the neutral oils come out with water, leaving resinoids and heavy hydrocarbons behind The temperature was then increased up to 350° Centigrade to obtain further fractions At this temperature only liquid pitch remains behind at the bottom of the flask This is now poured out, cooled and weighed The oils absorbed in their oil seals and those collected in the scrubber were distilled separately and the lightest fractions, boiling at as low a temperature as 60° Centigrade, were recorded and measured Analysis of the gas coming out of each specimen of coal was carried out by means of Prof. Junker's gas calorimeter This forms one of the most essential parts of our experiment and its usefulness will be well understood by fuel technologists.

It will be seen from our experimental results that the data about tar, oil and gas collected out of each sample of our coal had been also a check as to whether it was carried out under low temperature conditions or not. It is well known that the gas obtained from one ton of coal by the low temperature method is about 5,000 c ft while from the same coal by high temperature process we may get even 11,000 c ft The calorific value of the high temperature carbonisation gas is only about 500 B T U. whereas for the low temperature distillation gas a calorific value of even 800 B T U is quite common Hydrogen and hydrocarbons are predominant constituents of the high temperature gas but the low temperature gas is rich in saturated hydrocarbons All these have been very well borne out by the results of our experiments noted below

I *List of coals distilled*

(1) New Bansdeopur Colliery No 12 seam, incline No 15
(2) ,, ,, ,, ,, 11 ,, ,, ,, 14
(3) ,, ,, ,, ,, 10 ,, bottom of No 3 pit
(4) Godhur Colliery No 10 seam, No 1 pit
(5) ,, ,, ,, 9 ,, from near the Jore 10A incline
(6) Sendra Bansjora Colliery No 10 Coal seam
(7) ,, ,, ,, ,, ,, ,, ,,
(8) ,, ,, ,, ,, ,, ,, ,, (slack coal)
(9) ,, ,, ,, ,, ,, ,, ,, (,, ,,)
(10) Matigora Colliery—combined V, VI, VII seams (100 ft seam)
(11) ,, ,, No X seam
(12) ,, ,, Mixture 70% of 100 ft seam and 30% of No 10 seam

II *Results of Distillation test*

(1)

Amount of coal distilled	7 lbs	
Temperature of the furnace	525°C	
Products :—		
Coke (highly swelling hard coke), 6 lbs 1 oz	@ 17 32 cwts	per ton
*Tar oil (moist), 141·5 c c.	@ 10·06 gals.	,, ,,
Amm Sulphate	@ 6 62 lbs	,, ,,
Gas, 12 c ft	@ 3,840 c ft	,, ,,

Analysis of Gas

CO_2	2·41%
O_2	1·12%
Unsaturated	3 5%
CO	11 23%
CH_4	47·65%
H_2	27 90%
N_2	6·19%

Average calorific value of the gas is equal to 750 B T U

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* Measured under moist condition.

(2)

Amount of coal distilled	8 lbs.
Temperature of the furnace	520°C
Products :—	
Coke (moderately swelling coke), 7 lbs 0·5 oz	@ 18·28 cwts per ton
Tar oil (moist), 140 c c	@ 8·7 gals ,, ,,
Amm Sulphate	@ 7·02 lbs ,, ,,
Gas, 15 c ft	@ 4,230 c ft ,, ,,

Analysis of Gas

CO_2	2·93%
O_2	0·85%
Unsaturated	3·17%
CO	12·56%
CH_4	46·95%
H_2	28·32%
N_2	5·22%

Average calorific value of the gas is equal to 750 B T U

(3)

Amount of coal distilled	8 lbs.
Temperature of the furnace	535° to 540°C.
Products :—	
Coke, 7 lbs 2 ozs	@ 17·8 cwts. per ton.
Tar oil (moist), 144 c c	@ 7·9 gals ,, ,,
Amm Sulphate	@ 11 lbs ,, ,,
Gas, 11·9 c ft.	@ 3,332 c ft ,, ,,

Analysis of Gas

CO_2	3·23%
O_2	0·41%
Unsaturated	0·54%
CO	17·88%
CH_4	46·77%
H_2	22·77%
N_2	8·4%

Average calorific value of the gas is equal to 750 B T U

(4)

Amount of coal distilled	8 lbs
Temperature of the furnace	515° to 520°C.
Products :—	
Coke, 7 lbs. 0·5 oz	@ 17·58 cwts per ton
Tar oil (moist), 140 c c.	@ 8·71 gals ,, ,,
Amm. Sulphate	@ 8·41 lbs ,, ,,
Gas, 13·55 c ft.	@ 3,794 c. ft. ,, ,,

Analysis of Gas

CO_2	3·12%
O_2	0·96%
Unsaturated	2·57%
CO	11·55%
CH_4	47·68%
H_2	25·25%
N_2	8·87%

Average calorific value of the gas is equal to 750 B T U

(5)

Amount of coal distilled	10 lbs
Temperature of the furnace	515°C

Products —

Coke, 8 lbs 11·5 ozs	@ 17·44 cwts	per ton	
Tar oil (moist), 160 c c	@ 7·969 gals	,,	,,
Amm Sulphate	@ 23·95 lbs	,,	,,
Gas, 22 c ft	@ 4,928 c ft	,,	,,

Analysis of Gas

CO_2	2·58%
O_2	1·23%
Unsaturated	3·22%
CO	10·98%
CH_4	47·37%
H_2	26·32%
N_2	8·3%

Average calorific value of the gas is equal to 750 B T U

(6)

Amount of coal distilled	10 lbs
Temperature of the furnace	550° to 575°C

Products —

Coke, 8 lbs 8·5 ozs	@ 17 cwts	per ton	
Tar oil, 150 c c	@ 7·5 gals	,,	,,
Gas	4,600 c. ft	,,	,,
Calorific value	770 B T.U	(I).	
	744·7 ,,	(II).	
	722·8 ,,	(III)	

Analysis of Gas

CO_2	2·83%
O_2	0 809%
Unsaturated	2 97%
CO	7·15%
CH_4	42 0%
H_2	36 98%
N_2	7 26%
Ammonium Sulphate	14 lbs per ton

(7)

Amount of coal distilled	10 lbs
Temperature of the furnace	550° to 575°C
Products —	
Coke, 8 lbs 8 ozs	@ 17 cwts per ton
Tar oil, 150 c c	@ 7 5 gals ,, ,,
Gas	4,600 c ft ,, ,,
Calorific value	747 3 B T U (I)
	725 1 ,, (II)
	730 3 ,, (III)

Analysis of Gas

CO_2	4·724%
O_2	0·63%
Unsaturated	3·62%
CO	7·08%
CH_4	46 81%
H_2	32·22%
N_2	4·92%
Ammonium Sulphate	12 5 lbs per ton

(8)

Amount of coal distilled	10 lbs.
Temperature of the furnace	515°C
Products :—	
Coke, 8 lbs 14 ozs	@ 17 cwts 78·5 lbs per ton
Tar oil (moist), 170 c.c.	@ 8·46 gals. per ton
Amm. Sulphate	@ 5·8 lbs ,, ,,
Gas, 15·3 c. ft.	@ 3,427 c ft. ,, ,,

Analysis of Gas

CO_2	1·27%
O_2	1·2%
Unsaturated	2·52%
CO	9·3%
CH_4	48·2%
H_2	26·22%
N_2	11·3%

Average calorific value of the gas is equal to 750 B T U

(9)

Amount of coal distilled	10 lbs.
Temperature of the furnace	550°C
Products —	
Coke, 8 lbs 12 ozs	@ 17·5 cwts per ton
Tar oil (moist), 188 c c	@ 9·4 gals ,, ,,
Amm Sulphate	@ 10·5 lbs ,, ,,
Gas, 17·3 c ft	@ 3875·2 c ft ,, ,,

Analysis of Gas

CO_2	2·3%
O_2	0·406%
Unsaturated	2·17%
CO	14·49%
CH_4	48·57%
H_2	20·46%
N_2	11·6%

Approximate calorific value of the gas is equal to 750 B T U

(10)

Amount of coal distilled	10 lbs
Temperature of the furnace	525°C
Products —	
Coke, 8 lbs 8 ozs	@ 17·5 cwts per ton
Tar oil (moist), 143 c c	@ 7·12 gals ,, ,,
Amm Sulphate	@ 5·9 lbs ,, ,,
Gas, 16·5 c ft	@ 3,696 c ft ,, ,,

Analysis of Gas

CO_2	3·8%
O_2	0·9%
Unsaturated	3·5%
CO	7·2%
CH_4	45·4%
H_2	27·9%
N_2	11·3%

Approximate calorific value of the gas is equal to 750 B.T U.

(11)

Amount of coal distilled	10 lbs
Temperature of the furnace	525°C

Products :—

Coke, 8 0 lbs 9 ozs	@ 17 25 cwts per ton
Tar oil (moist), 175 c c	@ 8 71 gals ,, ,,
Amm Sulphate	@ 8 2 lbs ,, ,,
Gas, 26 7 c ft.	@ 5,980 c ft ,, ,,

Analysis of Gas

CO_2	4 24%
O_2	0 15%
Unsaturated	2 9%
CO	9 4%
CH_4	44 4%
H_2	26 83%
N_2	12 08

Approximate calorific value of the gas is equal to 750 B T U

(12)

Amount of coal distilled	8 lbs.
Temperature of the furnace	515°C

Products —

Coke, 7 lbs. 1 oz	@ 17 6 cwts per ton
Tar oil (moist), 120 c c	@ 7 47 gals ,, ,,
Amm. Sulphate	6 7 lbs ,, ,,
Gas, 12·9 c. ft.	@ 3,612 c ft ,, ,,

Analysis of Gas.

CO_2	5 59%
O_2	0 00%
Unsaturated	3 4%
CO	7 35%
CH_4	46·7%
H_2	27·4%
N_2	9·56%

Approximate calorific value of the gas is equal to 750 B T.U.

III *Tar oil fractions* (*i e* Fuel oil, etc) —

Sample No (1)

Up to 100°C *	11 3 c c	@ 0 8 gal per ton
100° to 135°C	12 c c	@ 0·85 ,, ,, ,,
135° to 150°C	8 4 c c	@ 0 59 ,, ,, ,,
150° to 210°C	10 1 c c	@ 0 72 ,, ,, ,,
210° to 350°C	56 c c	@ 3 98 ,, ,, ,,
Phenols	19 c c	@ 10 35 ,, ,, ,,
Pitch	18 gms	@ 12 8 lbs ,, ,,
Oil absorbed in paraffin oil-seal	6 2 c c	@ 0 44 gal ,, ,,

Sample No (2)

Up to 100°C	10 4 c c	@ 0 65 gal per ton
100° to 135°C	13 4 c c	@ 0 83 ,, ,, ,,
135° to 150°C	10 2 c c	@ 0 63 ,, ,, ,
150° to 210°C	15 8 c c	@ 0 98 ,, ,, ,,
210° to 350°C	58 0 c c	@ 3·6 ,, ,, ,,
Phenols	15 c c	@ 0 93 ,, ,, ,,
Pitch .	18 gms	@ 11 2 lbs ,, ,,
Oil absorbed in paraffin oil-seal	6 5 c c	@ 0 4 gal ,, ,,

Sample No (3)

Up to 100°C	8 6 c c	@ 0 535 gal per ton
100° to 135°C	4 8 c c	@ 0 3 ,, ,, ,,
135° to 150°C	4 4 c c	@ 0 274 ,, ,, ,,
150° to 210°C	12 4 c c	@ 0 772 ,, ,, ,,
210° to 350°C	48 5 c c	@ 3 018 ,, ,, ,,
Phenols	5 0 c c	@ 0 311 ,, ,, ,,
Pitch .	. 13 6 gms	@ 8 46 lbs ,, ,,
Oil absorbed in paraffin oil-seal	4 0 c c	@ 0 25 gal ,, ,,

Sample No (4)

Up to 100°C.	13 c c	@ 0 809 gal per ton
100° to 135°C	4·4 c c	@ 0 2738 ,, ,, ,,
135° to 150°C	4 6 c c	@ 0·286 ,, ,, ,,
150° to 210°C	20 9 c c	@ 1 301 ,, ,, ,,
210° to 350°C	64 8 c c	@ 4·032 ,, ,, ,,
Phenols	12 0 c c	@ 0 7469 ,, ,, ,,
Pitch .	18 0 gms	@ 11 2 lbs ,, ,,
Oil absorbed in paraffin oil-seal	6·3 c.c	@ 0 392 gals. ,, ,,

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* For properties, see end of this paper

Sample No (5)

Up to 100°C	14 5 c c	@ 0 7218 gal per ton
100° to 135°C	8 8 c c	@ 0 438 ,, ,, ,,
135° to 150°C	15 0 c c	@ 0 747 ,, ,, ,,
150° to 210°C	21 5 c c	@ 1 0702 ,, ,, ,,
210° to 350°C	62 0 c c	@ 3 0862 ,, ,, ,,
Phenols	7 0 c c	@ 0 3488 ,, , ,,
Pitch .	23 5 gms	@ 11 7 lbs ,, ,
Oil absorbed in paraffin oil-seal	10 c c	@ 0 5 gal ,, ,

Distillation of the tar —

Sample No (6)

150 c c Tar oil (treated with 5% NaOH)

Neutral oil distilled — Phenols 10 c c

Neutral oil distilled:

Up to 130°C	130°–150°C	150°–210°C	210°–350°C	Residual Pitch,
7 c c	12 5 c c	5 c c	35 c c	41 gms

Light oils dissolved in paraffin oil bottle distilled

Up to 90°C.	90°-130°C	130°–150°C
0·5 c c	2 5 c c	2·3 c c

Sample No (7)

150 c c Tar oil (treated with 5% NaOH)

Neutral oil distilled. — Phenols, 10 c c

Neutral oil distilled.

Up to 130°	130°–150°C	150°–210°C	210°–350°C	Residual Pitch,
8 c c	12 c c	8 c c	37 c c.	40 gms

Light oils dissolved in paraffin oil bottle distilled

Up to 90°C	90°–130°C	130°–150°C
0·5 c.c.	2·5 c c	0 7 c.c.

Tar oil fractions —

Sample No (8)

Up to 100°C	13 5 c c	@ 3 024 litres per ton
100° to 130°C	16 5 c c	@ 3 696 ,, ,, ,,
*130° to 150°C	11 2 c c	@ 2 509 ,, ,, ,,
150° to 210°C	13 7 c c	@ 3·0692 ,, ,, ,,
210° to 350°C	73 0 c c	@ 16 352 ,, ,, ,,
Phenols	15 0 c c	@ 3 36 ,, ,, ,,
Pitch	36 gms	@ 17 9 lbs ,, ,,

Sample No (9)

Up to 100°C	21 6 c c	@ 1 075 gals per ton
100° to 135°C	3 8 c c	@ 0 19 ,, ,, ,,
135° to 155°C	3 3 c c	@ 0 164 ,, ,, ,,
155° to 210°C	12 8 c c	@ 0 637 ,, ,, ,,
210° to 350°C	62 c c	@ 3 086 ,, ,, ,,
Phenols	14 c c	@ 0·7 ,, ,, ,,
Pitch	39 gms	@ 19·4 lbs ,, ,,
Oil absorbed in paraffin oil-seal	8 c c	@ 0 398 gal ,, ,,

Sample No (10)

Moist tar oil		@ 7 12 gals per ton
Up to 90°C	5 7 c c	@ 1 8 litres ,, ,,
90° to 130°C	8 c c	@ 1·792 ,, ,, ,,
130° to 150°C	21 c c	@ 4 704 ,, ,, ,,
150° to 210°C	4 2 c c	@ 0 9408 ,, ,, ,,
210° to 350°C	42 7 c c	@ 9 565 ,, ,, ,,
Phenols	9 9 c c	@ 2 218 ,, ,, ,,
Pitch	42 2 gms	@ 12 224 lbs. ,, ,,

Sample No (11)

Moist tar oil	175 c c	@ 8 71 gals per ton
Up to 90°C	5 2 c c	@ 1 165 litres ,, ,,
90° to 135°C	11 2 c c	@ 2 51 ,, ,, ,,
135° to 150°C	20 c c	@ 4·48 ,, ,, ,,
150° to 210°C	10 2 c c	@ 2·285 ,, ,, ,,
210° to 350°C	95 c.c	@ 21·28 ,, ,, ,,
Phenols	11 c c	@ 2 464 ,, ,, ,,
Pitch	19 gms	@ 9·46 lbs ,, ,,

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* This includes 8 c.c. of a fraction which has been dissolved in the paraffin oil-seal.

Sample No (12)

Up to 90°C	9 0 c c	@ 2 52	litres	per	ton
90° to 135°C	10 c c	@ 2 8	,,	,,	,,
135° to 150°C	14 2 c c	@ 3 97	,,	,,	,,
150° to 210°C	5 2 c c	@ 1 46	,,	,,	,,
210° to 350°C	53 0 c c	@ 14 84	,,	,,	,,
Phenols	8 0 c c	@ 2 24	,,	,,	,,
Pitch .	21 gms	@ 13 1	lbs	,,	,,

Average for Nos 6 and 7 Tar oil fractions —

Up to 90°C	0 112 litre	Motor spirit, per ton of coal
90°–130°C	2 352 litres	
130°–150°C	2 85 litres	Light oil, kerosene, per ton of coal
150°–210°C	1 8 litres	
210°–350°C	8 2 litres	Fuel oil ,, ,,
Phenols	2 25 litres (Carbolic acid and Creosote oil), per ton of coal	
Residual Pitch	19 7 lbs per ton of coal	

Difficulty is usually experienced in the carbonisation treatment of low grade coals either by low or high temperature methods These difficulties are due either to the high percentage of ash in these coals, or low binding power of its particles, or in some cases due to the presence of a considerable amount of binding material in the coal In the low temperature method if the coal does not possess sufficient binding property, the defect is rather of a serious nature because in that case the coke becomes very friable But the presence of a very large quantity of binding material is also sometimes rather inconvenient, especially when it is combined with a high swelling index of the coal Sometimes in such cases distillation becomes impossible The reason is, as has been explained before, that after the distillation has started the layer of coal immediately next to the hot walls of the retort melts and becomes frothy, this combining with the still unchanged coal lying next to it forms a solid non-conductive layer surrounded by a layer of coke from which most of the volatile matter has been expelled Conduction of heat in the interior of the retort from such a spongy mass becomes slow and before the above-mentioned solid layer of coal, formed by the mixture of plastic coal and undecomposed coal, becomes hot enough to melt, and again becomes frothy with the evolution of gas, a considerable amount of time is spent The plastic mass, together with particles of coal still lying undecomposed above it, is pushed all about the inside of the retort by the pressure of the escaping gases, whose pressure increases gradually due not only to the evolution of gases but also, usually, due to the choking of the outlet pipe by the plastic coal-coke Although we had started our experiments with a retort only half-filled with coal, in the course of time the whole of the interior of the retort becomes filled up with coke and coal When we extracted the coke of such coals we found that the coke was quite hard round the periphery while it was lighter and spongy towards the core This is due to the greater pressure to which the coal in the periphery was subjected by the evolving gases In the case of such coals, the distillation period becomes very much protracted and due to occasional choking of the outlet near about the end of the experiment, the volatile matter comes out slowly and spasmodically Therefore, in case of such coals, we were compelled to carry out our experiments with a smaller quantity than usual That is the reason why in the tables on pp 368–373 it will be found that some experiments had been carried out with 10 lbs of coal and others with a smaller quantity, our 'optimum quantity' in the retort The figures are inversely proportional to the degree of plasticity and swelling index of the samples For instance, we first tried to distil 10 lbs of our sample No 11 But scarcely had the distillation been continued for an hour, the gases and volatile matter started leaking profusely through the various joints of the retort while there was practically no flow of volatile matter through the absorbent system When this was the case, the distillation was discontinued and we had to find out a way to get over the difficulty

When the retort containing the products of our experiment was opened by removing the flanges, the whole of its inside was found to be filled up with a frothing, swelled, mass of partially distilled coal We were, therefore, obliged to find out the optimum charge of each of our samples by trial Thus it may be understood that we have carried out our experiments with optimum charges for our retort (see table on p 380) In order to determine the practicable quantity of each type of coal to be placed in the retort (so that satisfactory results may be obtained) we carried out the following simple experiments by means of which the amount of the optimum charge could be found out.

This is a modification of the method used by the research staff of the Woodalt Duckham Co (*Gas Journal*—'Coke Number'—November 9th, 1925, page 15) But at Woodalt Duckham Co 's laboratory the coal was tested by means of a button which was treated in an ordinary silicate crucible at 900°C In our case, however, we did not find this heating, right up to 900°C, quite satisfactory It gives sometimes misleading information regarding the swelling property of some of our samples, the reason being that certain coals swell at low temperature and do not look swelled so much at 900°C This is due to the fact that at a certain stage between its swelling points at about 500°–600°C, the coke collapses and at the higher temperature of 900°C we find it showing a much lower volume than at a lower temperature

Sometimes also a coke which may be swelling at 900°C may be quite non-swelling at 550°C For this purpose some preliminary experiments had to be carried out to avoid any serious breakdown in the middle of the experiment This preliminary experiment consists of the following :—

About one gram of the finely powdered coal was made into a loose tablet by means of a small screw compressor and this was placed in a small covered silica crucible. The crucible was then placed into a muffle furnace whose temperature was maintained at 550° to 600°C A reducing atmosphere was maintained round the crucible by putting a few pieces of wood charcoal within the muffle Violent evolution of gas takes place within a minute or two and the gas sets itself afire A flame is formed round the lid of the crucible This is watched through a hole in the door of the muffle The time of the evolution of the gas and disappearance of the flame is noted and even after the flame has died out the crucible is allowed to remain inside the muffle for a few minutes It is then taken out and the coke button in the crucible is examined for swelling properties As stated above, this simple experiment has helped us a good deal to determine the approximate amount of the coal to be charged in our retort for each experiment

The same experiment was also made to determine the most suitable blend of our samples Nos 10 and 11, for the low temperature carbonisation test Both of these are coking coals but their coke buttons behave very differently under different conditions For instance, the coke button of sample No 10 at 900°C shows very little swelling while that of sample No 11 was found to be of a very highly swelling nature Both of them formed coke No 11 again not only becomes a very highly swelling coke during low temperature tests but it becomes very plastic during the experiment In this plastic state it chokes the outlet and checks the evolution of volatile matter The plastic coal forms a spongy mass which on the surface has a frothy appearance As explained above in certain cases the frothy mass forms a non-conducting layer round the still unaffected coal powder in the crucible and develops a rather heterogeneous texture of the coke of the low temperature carbonisation process No 11 possesses almost double the plasticity and swelling power of sample No 10. For all these reasons sample No 11 alone is not very suitable for low temperature coking It can be used for high temperature practice, where the swelling of coke is not of much consequence and where a large quantity of gas is welcome. Sample No 10 does not show the plasticity and swelling of No 11 and the coke is hard and compact with little or no sponginess But blending of samples 10 and 11 reduces the excessive swelling tendency of the mixture during distillation A 50% mixture behaves almost exactly as pure sample No 11, and ultimately it was found that the best coke can be made out of these two coals by a mixture containing 30% of sample No 11 and 70% of sample No 10 Such a blend showed very little sign of plasticity and swelling, and the distillation period was much less protracted than that of sample No 11 The yield of volatiles was also more than that for pure No 10. The coke was fairly hard, compact and of uniform structure.

In the following table we have given a tabulated list of our samples showing the nature of their low and high temperature coke buttons, the nature of their cokes and the optimum distillation charge of each one of them for our own retort

Number of the coal sample	Nature of the low temperature coke button	Nature of the high temperature coke button	Optimum distillation charge	Nature of the low temperature coke obtained after assay
1	Normally caked fairly swelling	Slightly less caking and swelling than the low temperature button	7 lbs	Fairly hard compact structure on the surface with spongy internal structure
2	Caked and slightly swelling	Very little swelling and compact coke button	8 lbs	Fairly hard and compact coke with slight spongy internal structure
3	Caked and slightly swelling	Swelling more appreciable than in the case of low temperature coke button	8 lbs	Fairly hard and compact coke with slight spongy internal structure
4	Do	No appreciable swelling	10 lbs	Robust and compact coke
5	No appreciable swelling	Very slightly caking and swelling	10 lbs	Hard, robust and compact coke
6	Do	Slightly caking and swelling	10 lbs	Hard and compact coke with graphite surface
7	Do	Do	10 lbs	Do
8	Very slight swelling and caking	Non caking, mass apparently shrinks in size slightly	10 lbs	Do
9	Do	Do	10 lbs	Do
10	Very slight swelling and non caking	Very slight swelling and caking	10 lbs	Hard and robust coke
11	Very highly swelling and caking	Normally swelling and caking	5 lbs	Swelled coke with frothy surface appearance and spongy internal structure
12	Slightly swelling and caking	Do	8 lbs	Slightly swelled cokes fairly hard with very uniform internal structure

Properties of the Distillates

We hope it may not be out of place if for ready reference we add at this place some of the most important uses of the tar oil fractions as obtained from the coals treated by us

Distillation temperature up to 100°C. (*Neutral light oil*) —This fraction has all the properties of petroleum ether and solvent naphtha and mixed with the next fraction can be used as motor spirit.

Distillation temperature up to 135°C. (*Neutral light oil*) —This is equivalent to petrol or motor spirit as is obtained in the petroleum refineries.

Distillation temperature up to 150°C (*Neutral oil*) —This is equivalent to the lightest kerosene known as white kerosene obtained in the petroleum refineries

Distillation temperature up to 210°C (*Neutral oil*) —This is equivalent to heavy kerosene known as yellow kerosene obtained in the petroleum refineries

Neutral heavy oil —This fraction distilling between 210°–350°C has been considered as a whole The specific gravity of this fraction is 0 95 and flash point as determined by us is 171°C The last portion of this fraction, distilling between 300° to 350°C, possesses a greasy consistency. With a suitable blending material this can be converted into vaseline and lubricating greases Separated from the greasy matter, the heavy neutral oil becomes less viscous and as such can be suitably employed as fuel for the Diesel engines, or after cracking can be changed into motor spirit, lubricating oils, fuel or Diesel oils Hydrogen, hydrocarbons and carbon black can also be manufactured out of it

Phenol —This is the dark red liquid having a specific gravity 1 05 to 1·1 and possessing a strong creosotic smell obtained after the separation of the heavy oils It can be employed as a disinfectant or for creosoting timber, or it can be directly employed for Bakelite industry where such mixed phenols are necessary.

Pitch —The last residue of our distillation is pitch The uses of coal tar pitch are many and are constantly increasing

The gas obtained from our low temperature carbonisation experiment has a very high calorific value It can be economically employed for firing boilers for the generation of electric power As the problem of storing of such large quantities of gas has not yet been solved, it seems quite reasonable that its combustion in the boilers is so far the most profitable way of utilising the gas The gas can also be utilised in gas engines Nowadays even motor cars are running by such gas The start which the Government of Bihar has given in this direction needs special mention For the success of their newly conceived electrification scheme, they propose to generate power by firing their boilers with this 'waste' gas They have recently installed an experimental low temperature coking plant at the Science College, Patna, for conducting systematic researches with various samples of low grade Bihar coal The junior author, Mr. S S. Ghosh, M.Sc., is the chemist in charge of this plant. The main purpose behind this experimental plant is to make good smokeless domestic coke out of poor grade coals and recover the valuable by-products such as tar, ammonium sulphate and gases How far the gas can be utilised to generate power will also be investigated.

We are grateful to Dr. C S Fox, Director, Geological Survey of India, for his very kindly reading through the manuscript of this paper and making many useful suggestions.

Our thanks are due to Prof. B. C. Roy, M.Sc. (Leeds), of the University College of Science and Technology, Calcutta, for offering facilities for conducting these researches in his laboratory and also for many useful suggestions. Thanks are also due to Prof S K Bose, Indian School of Mines, Dhanbad, who rendered some financial assistance to prosecute the work and to Mr S K P Sinha, B Sc (Glasgow), Special Officer in charge Electrification, Bihar, for his keen interest throughout the research work

BRIQUETTING OF COAL IN INDIA

By C. Forrester,* *A H W C, F I C, Ph D, F R S E,*
Fellow of the Institute of Fuel.

This is a subject that, like that of the cleaning of coal, has not had given to it the attention, by practical men, that it appears to deserve Enormous quantities of Indian coals that are for one reason or another classed as 'waste' or 'low grade' are not satisfactorily disposed of, and the history of the coal-mining industry furnishes innumerable instances of such waste or poor-selling material being (usually temporarily) a drug on the market and presenting a serious problem to the industry Fluctuations in the requirements of the various grades and sizes of coals, as regards both quality and quantity, alter the aspects of the associated problems, but it will probably be admitted that the disposal of slack coal, even though it is not at present a specially urgent problem, has been a cause of great concern to the industry in the past and may be so again in the future.

So far as utilisation of slack coal is concerned the development of chain grates and automatic stokers as well as of pulverised coal has, of course, mitigated this evil There are times, in fact, when the smaller sizes of coal fetch a higher price than the larger. But there are coals in India that are so extremely friable that even locally their utilisation is not yet satisfactorily dealt with. Particular reference might be made to the coals of Assam and the Punjab These latter cannot be satisfactorily used on travelling grates, or at least not so satisfactorily as coals of better coking quality Their conversion into briquettes would appear to be one possible solution to an undoubted problem

But the briquetting of coals is a method of treatment that need not be confined to those friable deposits, and the possibilities of briquetting slack coal of the Raniganj and Barakar Series and of other Gondwana coals may yet become an important subsidiary industry.

What are the main problems ? They are : (*a*) selection of a binder and its cost, (*b*) selection of a process or of a type of briquette (the word is used in its most general sense).

Now the earliest type of binder used is the one that is still the most successful and the most favoured, namely pitch. There are many different types of pitch, *e g.* coal-tar pitch, petroleum pitch, etc. The latter is the best for consolidating small coal into a coherent form, as a smaller percentage is required than when coal-tar pitch is used, and coal-tar pitch does not give

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[Published August 20th, 1940.

such a good 'finish' to the product. But coal-tar pitch is much cheaper than petroleum pitch. In Britain the former costs about 30*s.* per ton (at present, 1939, on account of large surplus stocks, the price is as low as 21*s.* per ton). Petroleum pitch costs, in Britain, as much as 70*s.* per ton. One firm manufacturing small (ovoid) briquettes uses as little as 4½ per cent of petroleum pitch as against 7 per cent of coal-tar pitch. The total briquetting costs in the U.S.A. amount to about one dollar per ton, $1·06 is given as a recent average, which is equivalent to Rs. 3 approximately, the pitch accounting for Rs. 2-2-0.

The corresponding prices for India are not at present available. Unfortunately, therefore, it is not possible to offer reliable comparative figures for the process. But a year or two ago pitch was selling at about Rs. 35 per ton, and more recently the price has been as high as Rs. 58-8-0. Taking the lower figure and allowing for, say, 5 per cent of pitch for binding the small coal into coherent form we see that about 5 per cent (*i.e.* approximately one-twentieth) of Rs. 35 has to be added to the price of coal per ton to obtain the price of the briquette, without taking into consideration the cost of the process. An addition of approximately Rs. 2 per ton for binder alone is thus inevitable under present conditions.

What is the alternative? Theoretically there are several. One obvious one is to substitute, for coal-tar pitch, a cheaper binder. Many have been tried, and such substances as rice husks, bisulphite waste liquor from the paper-making industry, molasses, waste jute products, etc. are obvious suggestions. But nearly all these substitutes have been found to give briquettes that do not stand the severe tests of a tropical climate. The soft coke industry and perhaps the low temperature carbonisation industry, if it is ever established in this country, will probably offer a part solution to this problem by providing a cheaper pitch. The author favours the development of the soft coke industry along lines that would involve no very great departure from present methods other than to attempt to recover a substantial proportion of the tar. Even at the risk of adding to the present alleged surplus of coal tar it might be worth while rendering available larger quantities of tar to provide the necessary pitch. Whether the plastics industry will provide an outlet for the other distillation products and thus solve the parallel problem of their disposal only time can tell.

The obvious solution at present is to avoid the use of a binder entirely, *i.e.* to try to make briquettes without a binder and thus avoid adding this source of direct expense. Till recent years attempts to briquette coal without a binder have not met with much success. Six years ago the author personally investigated the claims of one promising process, but a short time after his return to India it was learned that the process had not been a commercial success. Later information (obtained privately a few months ago) is to the effect that methods for consolidating coals without a binder are now economically sound The more interesting and important fact, so far as India is concerned, is that certain Indian Gondwana coals are eminently suitable for the manufacture of briquettes without the use of a binder

The pressures used in this type of briquetting process vary within wide limits, as much as 20 tons per square inch being necessary to consolidate anthracites and anthracitic coals, but coking coal slack has been, and is being, successfully briquetted at as low a pressure as 1 5 to 2 tons per square inch But these lower pressures are generally found possible only by first heating the coal to the temperature of incipient fusion, *e g* about 450°C

Agglutinating long-flame and other high-volatile coals require a higher pressure, *e g* up to about 6 tons per square inch, accompanied by heating to the optimum temperature, usually a temperature ascertained within fairly narrow limits, from 400°C to 420°C

The great advantage of 'pure coal' briquettes, as these non-binder forms of consolidated 'smalls' are sometimes called, is their comparative smokelessness Pitch used as binder adds greatly to the smokiness of the product when burnt

So far as costs go, the pitch processes would appear to be more expensive than those employing high pressures and no binder Figures for manufacture of small briquettes ('ovoids') in England vary from as little as 5*s* per ton, using no binder, to 7*s* 6*d* per ton, using pitch But these figures must be accepted with caution as every head of expenditure in India gives rise to totally different costs Careful calculations made in very recent investigations show that the cost of making ovoids without the use of a binder would probably be approximately Rs 2-15-0 per ton (Private communication)

The other problem of selection of type of process is equally interesting The word 'briquette' means, of course, small brick and, by extension, brick-shaped article Originally briquettes were manufactured by consolidating extremely low-grade slack and dust coal into brick-shaped lumps and were used either on railways (as is a widespread practice in France and Belgium) or as a domestic fuel Some of the briquettes commonly used by railways on the Continent are two or three times the size of ordinary bricks and the name is no longer strictly appropriate These large brick-shaped briquettes offer the advantage of economy of space in storage, on account of their permitting regular stacking

At the other end of the scale we have the more recent development of the manufacture of extremely small lumps usually egg-shaped and known as 'ovoids' The present author strongly advocates the development in India of the manufacture (without the use of a binder, if possible) of ovoids for all purposes requiring a solid fuel whose combustion should be easily and, if necessary, scientifically controlled And ovoids present the special attraction that they will probably always be more likely to be successfully manufactured without the use of a binder than can the orthodox briquette.

There would appear to be scope for the development of a pitch-making industry in conjunction with the soft coke industry solely for the purpose of providing a cheap pitch for briquette-making and also for the manufacture of ovoids from small and dust coal without the use of a binder Recent investigations by experts have conclusively proved that Barakar and Raniganj coals are definitely suited for the processes.

BRIQUETTING OF COAL

By A N MUKHERJEE, *Dr -Ing , B Sc , A I S M , By-product Plant, Giridih, E I Ry*

Introduction.

Briquetting is the name given to an agglomeration of small coal, coke breeze, charcoal dust or bog turf together with some binding material consisting chiefly of coal tar or pitch According to Menzel,[1] the oldest record states that the ball-shaped compressed coal originated in China Hugh Platt[2] described in 1603, in a pamphlet, a new compressed fuel manufactured in the year 1594 in the neighbourhood of Lükeland in Germany, made of coal dust, saw dust and oak tan-bark, with cow dung as binding material The first coal briquette factories were —

In France, 1842, at Bernard, near St Etienne
In England, 1846, at Newcastle-on-Tyne
In Germany, 1861, at Mühlheim-on-the-Ruhr

In Europe, during the past 60 or 70 years, the briquetting industry has been developed and at present it has impressed its importance among the world's industries In the U S A , the expansion of the industry, with its increasing value in economising waste products, has been brought into notice very recently because the U S A has been so amply endowed with excellent mineral fuels that very little attention was given before to the utilisation of coal waste, screenings and other combustible matter in their manufacture into briquettes

Evidently, this industry is in its most advanced condition in countries possessing large areas of inferior qualities of coal or with broad localities of peat bogs and where fuel is high-priced. It has also been largely developed in the countries in which by-product coke oven plants are in use producing coal tar which can be used in its crude form or distilled to pitch, thus contributing the important binding material in the manufacture of briquettes It may be noted in this connection that in most of these countries in which the briquette industry has been developed the price of coal is very high To insure a market for the briquette products, the price must be considerably lower than that of good coal in the several briquette-producing countries

At the time, Germany[3] is the largest producer of briquettes and with the development of this industry there has been invented many varieties of briquetting machines Briquettes form the principal domestic fuel of Berlin and other cities and districts in Germany. They are used in locomotives and other steam fires and are employed for heating in various processes of manufacture German briquette factories are divided, in respect to the crude material employed, into two general groups: those that make household briquettes

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from brown coal (lignite) or carbonised peat, and those that produce the so-called 'Industrie Briquette' using as basic material coal dust or slack household briquettes, as made in Germany from brown coal or peat, and used in grates, heating stoves, cooking stoves and ranges They are cheaper in Germany ton per ton than good bituminous coal Industrial briquettes are used in Germany for firing locomotives and other steam boilers, for smelting and reverberatory furnaces and for many other kinds of industrial use

The manufacture of coal briquettes known as patent fuel is not conducted on a very extensive scale in Great Britain In the establishment of briquetting plants in the U S A and also in Canada the same degree of success has not materialised as in Europe This is mainly due to the difference in the available fuels and their method of utilisation in Europe

France, Belgium, Austria, Hungary, Netherlands, Norway, China and Japan have also taken up the manufacture of briquettes in a small way

Fuel briquetting has for its aim the accomplishment of the following objects —

(1) The utilisation of the fine material (slack coal) unavoidably made in the mining and handling of coal
(2) The creation of a good hard fuel to burn practically without smoke or odour
(3) The concentration of the greatest number of heat units into the smallest space practicable, by cleaning and compressing material of inferior heating value

In the mining of coal, a large proportion of the output of a mine is often necessarily dust, slack or culm, of which a certain amount is wasted In the case of coking coals, the slack is generally charged into ovens, but dust of other coal is usually wasted

The advantage of using fuels that burn without smoke or odour is very great, especially in big cities where dense trailing clouds of smoke coming out of the chimneys of mills and factories pollute the atmosphere To appreciate the advantage of using the briquette or patent fuel, one should contrast some American cities or English towns with those of Germany where the briquette is largely used for industrial and domestic purposes

The third object—that of obtaining concentrated fuel—is very important from a national point of view in a country in which large deposits of inferior quality of coal occur. This coal can be very economically used in the manufacture of briquettes which will burn practically without smoke and produce more calories of heat than produced by the raw fuel

Briquettes are made in various shapes and forms They are made in sizes varying from 20 pounds each to a size that takes several to make a pound Industrial briquettes are usually of a square or oblong form, convenient to be packed or built up into a pile like bricks. The domestic briquettes are generally of smaller sizes varying from ½ pound each to 2 pounds and they are of egg-shape or oval-shape.

The fuel briquette should satisfy the following specifications: it must be hard, homogeneous in density and size and only very slightly hygroscopic and should burn almost without smoke or odour, the breakage caused by handling should not exceed 5%, it should ignite readily and retain its shape when completely burnt.

Methods and Costs of manufacturing Briquettes

Briquettes may be made of any one of the following materials: Coal slack, screenings, or dust, anthracite screening or culm, coke breeze or small coke, lignite coal, charcoal, peat or torf, petroleum. The method of manufacture may be divided into two general groups:

(1) *Briquetting with binding material,* where the coal or coke must be compressed with bonds in order to manufacture briquettes. The binding materials used for binding together the small particles of fuel employed in making briquettes are various, amongst them being asphalt, coal tar, pitch, petroleum, molasses, magnesia cement, starch paste, etc.

The most common binder used is pitch in its various forms. The hard pitch[4] used for briquetting should contain 75% to 80% of carbon and only 25 to ·5% of ash. Though tar and soft pitch are also used as binders, they have many disadvantages which do not apply to the same extent to hard pitch. The presence of the light and heavy volatile hydrocarbons in the tar and pitch creates smoke and smell when this binder is used in briquettes, also, the point of distillation of soft pitch is about 400 degrees fahrenheit, while that of hard pitch approximates 800 degrees fahrenheit. Thus briquettes made with soft pitch have to be kept cool or they will soften and, by sticking together, form large lumps. Among the other organic binders, the most important are starch paste and sugar molasses, but these have not as yet attained more than local importance.

The most suitable inorganic binder is magnesia cement, which is both cheap and abundant. The use of 5%[5] of this material is said to produce a stronger briquette than that made by any other binder, when 5% of this binder is used, the quantity of ash added amounts to but 2 5%. The process of using magnesia cement is very simple and cheap, as no drying is required and the only fuel expended is that for power. The briquettes harden gradually at the ordinary temperature, and after from 6 to 10 hours are strong enough to be stored or handled, in a few days they are capable of standing a pressure of from 7,000 to 22,000 pounds per square inch. But on account of the higher ash content it is not preferred in the market wherever good hard pitch briquettes are available.

The manufacture of briquettes includes coal crushing, wasting, and drying processes[6]

First, the coal must be thoroughly cleaned and separated from all extraneous matter, the cleaner the product, the higher the value of the briquettes.

Drying is done in some instances in drying furnaces These furnaces being especially employed for coal that is of a semi-bituminous nature, because it becomes slightly softened and in such cases the pitch is introduced either immediately before or after the coal has passed through the furnace thus reducing the quantity of pitch required

The next process is crushing the coal This is done either by rolls, stone breaker or other disintegrator It is very important that the coal should be reduced to a uniform size The most satisfactory results are obtained from coal of an even size ($\frac{1}{8}$ inch) or from slack The finer the coal the greater is the quantity of pitch required to agglomerate it

When the wet or melted pitch process is employed the pitch is commonly mixed with 10 to 15% tar In cases where the dry pitch process has been adopted, the pitch is broken in a mill or cracker, then added in suitable quantity to the coal and the mixture is passed through a disintegrator An intimate blending of the two ingredients is thus ensured The mixture whether it has been heated in a furnace or not is finally heated in a heater or pugmill to render it perfectly pasty The heat is obtained either by a steam jacket, which is called the 'dry heat system', or by direct injection of the steam into the mixture which is called the wet steam process or by a combination of the two The temperature of the paste in the moulds of the press should not be lower than 70 degrees centigrade nor higher than 90 degrees centigrade The amount of pitch required as binding material varies with its quality, character, and quality of coal and its shape of division and with other circumstances which cannot be well determined except by experiment On the Continent the average is 5 to 9% and in Great Britain 8 to 10%. The average amount of water present in the paste should not be less than 3% and not more than 5%.

The presses used for briquetting are of various types There are two general types which are mostly in use: the press with open mould and the press with closed mould The closed mould type is divided into two classes tangential press and plunger press A large number of these presses are in operation making briquettes of all sizes. The pressure used depends on the quality of coal and binding material employed If the coal is soft and large, a light pressure will suffice. If a fine coal is used, the pressure ought to be heavy Light pressure can be used for molasses, as well as when a great amount of pitch is used for agglomeration.

(2) *Briquetting without binding material*—This process consists in manufacturing compact briquettes from coal dust or slack coal by pressure, such coal must contain 5 to 12% of water and high bitumen or resin content. Considerable attention has, in recent years, been devoted to the briquetting of coals without binder or with a small proportion of binder and presses that would give these results with a reasonable pressure, have been designed.

A notable briquetting process was patented by E R Sutcliffe [7] (British patent No 5108) This invention consisted in reducing the coal to a very finely divided condition, as would pass through a 200 mesh and compressing the raw material so as to produce a hard homogeneous and stonelike briquette In this process homogeneous briquettes from blends of coal have been made without the aid of a binder, subjecting the coal to a pressure of about 10 tons per sq inch The briquettes are subsequently carbonised at temperatures varying from 400 degrees to 1,200 degrees centigrade The advantages to be derived from briquetting, as a preliminary to carbonising and gas-making, are many Improvements in heat conductivity, the prevention of expansion and sticking troubles and increased yield of volatile products are some of the advantages accruing from briquette carbonisation

Some instructive experiments on carbonisation of briquettes were carried out at the works of the South Metropolitan Gas Company The briquettes from a blend of 75% of Durham coal with 25% of coke breeze were carbonised at high temperature and the results compared with those obtained when using 100% of the same Durham coking coal The results shown in the following table were obtained :—

Yields from Durham coal and briquetted mixtures [8]

Yields	Ordinary coal	Briquetted mixtures	
		A	B
Gaseous therms per ton of coal .	74 7%	68 2%	71 1%
Tar therms per ton of coal	16·1%	31 1%	27 5%
Total volatile therms per ton of coal .	90 8%	99	98 6%

The total yield of therms as a result of briquetting has increased nearly 9 per cent

Cost of making Briquettes [9]

The cost of making briquettes or patent fuel varies greatly, according to the location of the plant and the kind of material used. Plants are usually equipped as follows: One set of chain elevators; one pitch cracker; one mixer for mixing the coal and the pitch (or any other binding material) in the proper proportion; one disintegrator for pulverising the coal and pitch, one vertical heater; one briquette machine; steam engine; other necessary arrangements for driving the various items of the plant The average capacity per day of the plant depends entirely on the number of machines in use In some plants not more than 40 to 50 tons of briquettes are made per day of 10 hours, while in more elaborately equipped plants 100 to 120 tons of briquette are turned out in the same number of hours The estimated cost of manufacturing briquettes including raw material, labour, and interest on money invested, is about 25 shillings per ton in England and 9 to 10 marks in Germany

Briquetting of Coal in India

Briquetting of coal is not done in India In many parts of our coal-producing districts, immense stocks of unused fine coal has been wasted This material affords, when washed, the best substance for the manufacture of briquettes, especially for domestic purposes Next to the slack coal waste, the waste of coke breeze at the coke plant offers very desirable material for the manufacture of briquettes About 2 to 3% of breeze is made in the manufacture of coke As India produced in the year 1935, 1,759,036 tons of hard coke, the amount of breeze at the low estimate of 2% would be 36,000 tons of clean coke dust for briquetting All or nearly all of this is at present wasted It is quite probable that this coke breeze could be secured for the removing of it from the coke works or at most at a mere nominal price Briquettes could therefore be made at a moderate cost These briquettes would be very nearly smokeless, the only smoke-producing substance being the pitch used as binding material

Much of the inferior quality coal of India could be manufactured into briquettes with a minimum percentage of the binding material

The reason sometimes given by our industrialists for not turning their attention to the manufacture of briquettes in India is the scarcity of pitch and the cost of manufacture which will be higher than the price of other fuels available in India It should be noted that almost any resinous or tarry matter may be used as binding material for making briquettes Molasses acts as a good binder and is available in large quantities in India at a very moderate price At present it is either wasted at the sugar plant siding or sold at a nominal price

The estimated cost of manufacture of briquettes in India including raw material, labour and interest on capital invested, will be about 3 or 4 rupees per ton. The cost of a briquette plant with a capacity of 40 tons per day of 10 hours will be approximately 7,000 pounds in India [10]

It is to be hoped that immediate attention will be paid to the utilisation of the inferior quality of coal of India, slack coal and coke breeze, which have very little demand in the market and are wasted, for the manufacture of briquettes The briquette industry will not only solve the problem of economic utilisation of the neglected fuel resources of our country but it will also solve the smoke nuisance problem of our cities

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THE UNDERGROUND GASIFICATION OF COAL

By CYRIL S FOX, *D Sc*, *M.I Min E*, *Geological Survey of India*

The subject of the underground gasification of coal has been receiving a great deal of attention in the U S S R for the past five years and although two years have now passed since I was in Russia and made personal enquiries, there has still been no report of the process operating in an established manner.

It will be of interest to review the history of the Russian efforts They claim that Mendeleyev recommended the idea independently of the English chemist Sir William Ramsay who is believed to have suggested this method of using coal As I have not seen the original reference I am unable to say what was suggested.

The Russian experiments, so far as I could gather, arose in a logical way as a result of necessity Owing to a great shortage of wagons they found considerable difficulty in supplying the demand for coal for various important industrial centres and power stations for manufacturing plant

The policy they adopted was to send coal by train to the more distant consumers and to prepare gas at the collieries and pipe this fuel to the nearby steam-raising plant The success seems to have been complete as Moscow was to be supplied with gas in this way from Tula, 100 miles away.

Many ideas have followed for the complete gasification of coal at the collieries where producer and other gas works were established for the generation of gas and plans were made for elaborate distribution of this gas by pipe lines to the power stations where the gas is burned under boilers

The idea of having the gas producers at the bottom of shaft, that is underground instead of on the surface, was obvious as this would save the haulage of the coal and the disposal of the clinker and there would be some economy in expenditure to say nothing of the novelty of the thing

The zeal to do better and better with regard to bold schemes is a feature of Soviet Russia and so Mendeleyev's idea was revived and the astonishing daring of the operation made it a popular thing and thus it seems that permission was obtained to burn the coal *in situ* for gas.

All the details I was able to secure show that complete gasification of the coal seam is aimed at but I was unable to arrange a visit to any of the Podszen gas plant. It was explained to me that it was essential to have absolute control over the air and steam supply and gas produced.

From what I could gather the investigations are being made in coal seams which are relatively thin compared with what we have in India, and it is evident that there must be no old workings or breaks and faults through which the gas can escape into the adjacent workings or to the surface.

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When I think of the 24-foot and thicker seams in India and the large percentage of coarse sandstones which overlie the coal seams and remember the ease with which water percolates in the joints of the strata in the Gondwana coalfields I cannot imagine how gas cannot escape

If any proof was needed that underground gasification of the coal, as it stands in the seams, is likely to be a failure in India, owing to the ready escape of the gas through the porous sandstones and the points and fault planes, it is clearly before us in the Damodar Valley coalfields

You will remember the numerous peridotite dykes and the large areas of so-called 'burnt' or coked coal in many seams in the Jharia field and elsewhere, and the estimate that many millions of tons of coal had been spoilt by igneous intrusions which have produced natural coke

Have you considered how much gas must have been distilled by the coking of the coal? Where has it all gone? We do not even find any good evidence of the liquid products of distillation And yet that coking was effected in the virgin seams long before an incline was driven or a shaft sunk

I do not mean to imply that the gasification of coal in proper producers is not feasible underground in Indian collieries especially in poor quality coal seams but I believe the total thermal units which the gas could provide will be less and cost more than what could be secured by using the coal in pulverised form

However, these are aspects for closer consideration in power generation and it is quite possible that complete gasification of coal in properly constructed gas producers may be efficiently performed and the gas piped away to nearby consumers or supplied to a great electrical power station at very cheap rates

It is a question of the cost of the powdered coal and efficiency of the boiler combination on one hand against the cost of the gas and the efficiency of boiler combination on the other hand—*i e* on the cost of the powdered coal for doing the same work as the gas fuel at a given cost

DOMESTIC COKE

By N N. CHATTERJEE *

As a result of the recommendation of the Noyce Committee the Coal Grading Board was established by the India Government for grading coal A few years later the Soft Coke Cess Committee was formed and the Act No VIII of 1929 provided for the levy of a cess of two annas per ton on soft coke despatched by rail from collieries in the provinces of Bengal, Bihar and Orissa The purpose for which the cess was levied was two-fold, namely (i) for promoting the sale, and (ii) for improving the method of manufacture of soft coke The realisation of this cess has been going on for the last ten years and the fund thus accumulated is disbursed according to the scheme of expenditure formulated by the Soft Coke Cess Committee In the following pages an attempt is made to show how far the objects for which the cess was levied has been fulfilled

A perusal of the balance sheet published by the Soft Coke Cess Committee will show that practically all the money, *i e* nearly one lac of rupees, is spent for propaganda work in order to popularise the soft coke amongst the general public throughout India For the second object a sum of Rs 2,400 only was spent by the committee

A reference to the report will show that continuous propaganda has been carried out for popularising the soft coke and the detailed method of such work is quoted below

> 'The committee's staff made house to house visits in every centre and explained to householders the advantages, economic and hygienic, of soft coke over other fuels Practical demonstrations in lighting soft coke were also given whenever required Soft coke and portable ovens were distributed free at all propaganda centres ' 'The lady officers of the committee worked amongst the womenfolk with great success. The staff rendered all possible help to consumers in obtaining their supplies of soft coke Certain staff was also sent to outstations to carry on propaganda work ' . . 'The committee's publicity work was carried on through newspaper advertisements, distribution of handbills and leaflets ' . . . 'Pictorial posters were displayed at all propaganda centres and other towns ' 'Enamel signs were exhibited at important stations on all the principal railways. The committee's films were shown free to the public ' . . . 'Sandwich boys carrying posters and literature on soft coke paraded on suitable occasions.' 'The committee issued a calendar for the year 1938' and also for 1939.

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This speaks well of the energetic effort of the committee to push the sale of soft coke but I do not understand why the committee failed to realise that the commodity for which they are trying so much should also be improved in quality so that their efforts in popularising it might meet with success in a more easy manner They do not seem to have exerted much of their energy in this direction The consumers have been paying the cess for these years under the expectation that they would get a better commodity in return for the extra money spent, but ten years have elapsed without bringing about any change or improvement in the quality of soft coke and at the present day the same old material prepared by the same old process from the inferior grade and stony coals is placed on the market for which so much propaganda is carried out Sufficient length of time (ten years) has already elapsed, and if the method of manufacture of soft coke is not going to be improved and if a better quality smokeless fuel is not going to be placed on the market I do not see any reason why brisk agitation should not be started and why the India Government should not be moved to reduce the cess to a minimum or to stop it I am personally of the opinion that the first and foremost duty of the Soft Coke Cess Committee should have been to improve the coke in quality and then to carry the propaganda work for pushing its sale A reference to the report will show that the committee found their way to sanction the grant of a bonus on the sale of soft coke to depot-holders in Bombay but I think the committee would have acted more wisely if they awarded a bonus to the manufacturers of soft coke for producing a better smokeless fuel By this move the owners of coal mines would have taken the initiative to devise ways and means to improve the method of preparing soft coke Another suggestion is that the committee should make arrangement to check from time to time the quality of coke produced at different places and class them in different grades of quality and market prices The committee should give more attention to this aspect of the question and it is rather unfortunate that during the last ten years nothing has been achieved in this direction.

Method of Manufacture

A reference to the report shows that after ten years the committee realised that 'there is also room for improvement in the process of manufacture' and with a view to ascertaining how a better quality coke can be obtained the committee solicited the help of the '*Research Department of the Indian School of Mines*' and that groups of collieries were placed in charge of the local sub-committee and the '*Director of Fuel Research*', Indian School of Mines. We are not aware if there is any officially recognised department styled as '*Research Department*' in the School of Mines and of the personnel of that department

For the last few years a small amount of money has been placed at the disposal of the 'Research Department' of the Indian School of Mines to carry on research work to improve the method of soft coke manufacture A perusal of the report will also show that as a result of the so-called Research Department's investigations some very useful information on the manufacture of soft coke has been recorded But what this 'useful information' is nobody is aware of and it is to be regretted that this useful information could not find place in the report and be made public A few data are, however, published with regard to volatile matter and ash percentage of some soft cokes. These figures, without giving the names of the coal seams from which the soft cokes have been made, do not appear to be of any use except that they show the wide range of variation in the quality of soft coke

The description of the soft coke prepared in India as given in the report (page 5) shows that it is nothing but a mass of charred coal, half-burnt coal, and more or less completely burnt coal The report further admits that the quality of soft coke supplied by many collieries is often inferior. Stony coal is occasionally used in the manufacture The method of manufacture has been going on for a very long time without any improvement or modification The analyses that appear in the report amply demonstrate the poor nature of the majority of soft coke and that there is a very wide range in quality, some are practically unburnt and some are more or less completely burnt

It was felt by the committee that the work of improving the quality of soft coke should be of a more practical nature and that arrangements were made with colliery owners to carry out practical tests but nothing is made known as to the fate of such tests According to the report 'the trouble is to get manufacturers to recognise the importance of quality and one of the difficulties with which the committee are faced is that dealers do not buy on any specifications and consumers are only too eager to purchase in the cheapest market' It is really very strange to follow this argument that the manufacturers for whose benefit cess is collected and for whose commodity so much propaganda work is being carried on do not recognise the importance of quality In that case there should be no other alternative but to stop the cess altogether and the committee should dissolve forthwith Regarding the other point it may be said that when a better grade smokeless fuel is produced and placed on the market the dealers and consumers will gradually take to the better commodity even at a reasonably higher price. This is amply demonstrated in every type of business.

I take exception to the report saying on page 16 that 'in burning very little smoke is given off', etc. while enumerating the advantages of soft coke. The analytical results published in the same report on page 6 go to contradict this statement and it is really unfortunate that such statements should be used. When a soft coke of better quality is produced it will surely have a ready sale with less propaganda.

The requirements of a good domestic fuel should be as follows:—

(1) It should have been previously treated for the recovery of by-products from the raw coal and so rendered smokeless.

(2) It should contain only a small amount of volatile, say 7 to 10 per cent, and be of such structure as to be easily kindled and kept alight in open fire-places and should require very little draught for combustion
(3) Its radiant efficiency should be high
(4) It should be dense and compact so as to minimise transport and delivery charges and require a minimum storage space
(5) It should be sufficiently robust to stand normal handling and transport
(6) The ash should be low depending on the nature of the coal from which soft coke will be made In Bengal and Bihar coalfields we cannot expect low ash domestic fuels
(7) It should require minimum attention during combustion
(8) Its texture should be uniform
(9) The price should be sufficiently low to attract purchasers

The manufacturers of domestic fuel should try to obtain all these properties in their finished product A reference to the literature on this subject will show that many patents have been taken out to carbonise the coal at 600°C to obtain a smokeless patent fuel commonly known as *coalite* or *semi-coke* The best procedure, however, would be one in which arrangements are made for the recovery of common by-products such as tar, ammonia and gas The installation of a low temperature carbonisation plant or a Parker plant or a similar one with the arrangement to recover by-products would be an ideal thing no doubt but it need not be discussed here as there is hardly any scope to erect one at the different small collieries to use exclusively their inferior grade coals for the manufacture of semi-coke If, however, the scheme for obtaining liquid fuel and other by-products out of Bengal and Bihar coals proves satisfactory and favourable then the residue left behind in the retorts will be obtained as an ideal smokeless fuel far superior to the low grade soft coke now marketed and it is sure to capture the market and replace the latter

The question immediately before us, therefore, is to produce a better soft coke as domestic fuel from the inferior grade coals The manufacture on an economic basis of a semi-coke having many of the properties mentioned in a previous paragraph involves a certain amount of research. Investigations in the following lines are necessary. Blending of different seams in certain proportions, suitable size of the coal particles to be blended and carbonised, and the amount of excess binding material in the caking coal to be available for taking up non-caking coal and uniform cellular texture of semi-coke and so forth

Research work in some of the above useful lines has been in progress in the Geology Department, Presidency College, Calcutta, under my guidance and the results may be made available at an early date. As an example it may be said that the seam No X of western Jharia side may take up as much as 30% and seams VI, VII, VIII may take up 20% of some non-caking coal such as seam No IV Experiments with different sizes of coal particles show some variation in the capacity of blending Practical tests in the above lines will have to be carried out for guidance in the process of manufacture. After having sufficient information on these points the next step is to improve the actual process of manufacture It must be admitted by all that the method practised at the present day in burning coal in heaps requires immediate modification It has already been overdue Following this system it is impossible to get coke of uniform quality and wastage is also very high. Improved method of destructive distillation of coal out of contact with air has become imperative The author has visited many places in the Bengal and Bihar coalfields where soft cokes are manufactured and, as a result of his experience, he suggests that simple chamber ovens, such as beehive or rectangular chambers, may be suitably constructed for the purpose with ordinary brick but having an inner lining of firebrick There should be arrangements to allow for expansion that will occur during low temperature carbonisation but research work will help in avoiding unusual expansion There may be a movable iron framework at the bottom of the chamber to receive the coal charge and after the operation the coke may be raked out Simple chambers may easily be constructed to carry out carbonisation without any access of air at low temperature (500°C to 600°C) without any arrangement for recovery of by-products and gases This simple method will give a much better coke than what is manufactured at present The manufacturers should be encouraged to install chamber ovens with suitable arrangements to recover some of the by-products and gas There should also be simple arrangements for heating by burning gas in the flues and combustion chamber and also for recovery of gases The author of this note has prepared a sketch of one such chamber oven which will be published elsewhere Colliery owners and those who are manufacturers of soft coke should immediately start small experimental chamber ovens to carry out the practical tests The temperature should be regulated at will and should be in the neighbourhood of 500-600°C The period of heating is to be actually determined by trials and should be well within 24 hours Of course, it depends on the nature of the ovens and the amount of the charge, the size of the coal particles, moisture content, etc The coke thus produced will have a more uniform nature and quality and will be a suitable smokeless fuel for domestic use When generally adopted a large amount of useful materials such as tar, ammonia, etc will be made available for our different uses One will be surprised to know that about 0 75 million gallons of motor spirit, 1·5 million gallons of light oil (kerosene), 3 million gallons of lubricating oils, 0·75 million gallons of carbolic acid and creosote oil, 10,500 tons of ammonium sulphate, 15,000 tons of residual pitch and about 7·5 billion cubic ft. of very rich gas are at present being wasted during the annual soft coke making from the Jharia coals only (see S. K Roy—Presidential Address, *Proc Ind Sc. Congress*, 1939, p. 72) Attempts to install chamber ovens with arrangements to recover some of these by-products will save some valuable material from being lost and this will be a move in effecting the conservation of a national asset to some extent

The Soft Coke Cess Committee would act wisely if they carry on some propaganda work to induce the manufacturers of soft coke to adopt suitable blending of different coal seams and to use chamber ovens for low temperature carbonisation process so that better quality cokes may be placed on the market. The committee should be moved to award several prizes and to offer a substantial bonus to those manufacturers who take to improved methods of manufacture These prizes and bonuses may be fixed on a sliding scale according to the nature and stage of improvement Immediate and serious attempts should therefore be made by the committee to move in the matter as such an improvement in the soft coke manufacture has long been overdue and continued research on the lines already suggested will help the manufacturers in the proper selection and blending of coal seams, in having suitable size of coal particles for carbonisation and in other ways to impart good physical properties

The author also suggests that small colliery owners should combine and form bigger concerns and economic units so that better methods and plants with full scientific equipment might be easily adopted for the manufacture of smokeless domestic fuel on a bigger scale. The recovery of by-products may then be a simple and easy affair to tackle The author sincerely hopes that the Soft Coke Cess Committee will spend sufficient money to encourage and help the enterprise in this direction which is of fundamental importance

DOMESTIC COKE IN INDIA

By C Forrester,* *A H W C , F I C , Ph D , F R S E , Fellow of the Institute of Fuel*

The subject of 'Carbonisation of Coal' is dealt with separately in this *Symposium* and as it presumably covers the general question of low temperature carbonisation, such matters as the production of smokeless fuel by modern low temperature carbonisation processes are not dealt with in this short note

Domestic fuels in India comprise five main substances, namely, cow dung cakes, wood, charcoal, gas coke and 'soft coke' Of these the first three are ubiquitous, and the use of the last is to some extent limited either according to cost or according to suitability for the purpose for which it is required The first temptation of the fuel technologist in India is to assume that all that is necessary to deal with the triple problem of the provision of a good domestic fuel is to replace cow dung, wood and charcoal with one or other of the easily-ignited cokes The expression 'triple problem' is used as there are three important aspects of this matter that engage the attention of the enthusiastic scientist, namely—

(*a*) desirability of saving cow dung and other waste animal products for fertilisation of the land,

(*b*) desirability of providing inhabitants of cities with a comparatively smokeless fuel, and

(*c*) designing stoves, *chulhas*, etc and utensils suitable for use with the new type of fuel

The author has for some years been personally concerned in the investigations of the Soft Coke Cess Committee into methods used for manufacture of soft coke, with a view to discover to what extent, within the financial limitations of the industry, those methods can be improved Certain facts have been ascertained regarding the quality of the coal selected for manufacture of this form of domestic coke and of the product. The funds available did not permit of large-scale experiments being carried out and the author relinquished the funds a year or two ago pending a decision as to the sanctioning of expenditure for testing large-scale tar recovery processes. Preliminary results have, however, been published along with detailed information about the conditions obtaining in the heaps and the methods adopted for supervision of the process

In the course of these investigations he has also had to examine cokes of the type sold by the city gas corporations and to compare these alternative domestic cokes with the so-called 'soft coke'.

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VOL. VI—No. 3. [Published August 21st, 1940.

The problem of obtaining a comparatively smokeless fuel is one that brings in its train the equally important one of ensuring that the fuel shall be easy to use under ordinary domestic conditions Unfortunately the one desideratum can be obtained only at the expense of the other The reasons why some forms of carbon such as the various cokes are more easily ignitable than others have not yet been satisfactorily elucidated For the time being the important, and easily understood, fact is that quite apart from the *form* of the carbon (*i e* whether 'amorphous' and dull black or graphitic and more or less silvery) its association with a reasonable amount of volatile combustible matter aids in ensuring ease of ignition What minimum and maximum amounts of volatile matter are to be fixed has not yet been determined Samples of city gas corporation cokes largely used for domestic purposes in India showed the presence of from over 2½% of volatile to as much as just under 7% Enquiries regarding the suitability of these cokes for ordinary domestic purposes have shown that although they have proved entirely acceptable as smokeless fuels their ignition has frequently presented difficulties Comparison with a large range of soft cokes and practical experiments prove conclusively (as might, of course, be expected) that the larger the amount of volatile matter left in the coke, the easier it is to ignite But when we examine soft cokes we see that we sometimes come across samples that prove to be undesirably smoky in the earlier stages of their combustion

The problem, therefore, is to discover what compromise can be effected so far as volatile matter content is concerned and how it is to be attained There is the associated problem of trying to recover part at least of the volatile matter that is at present allowed to go to waste and to pollute the atmosphere of the coalfields where soft coke is made

The Indian soft coke industry has been built up, of course, on the utilisation of low grade coals and to that extent it may be regarded as fulfilling an important function in this country and going far towards assisting in conserving and fully utilising our coal resources No pretence is made that the coals used for the purpose are of high grade or that the product is a high grade one either. Any attempt to compare soft coke as made at present in India with domestic smokeless fuel as manufactured by modern low temperature carbonisation plants is not only absurd but also a waste of time And any proposal to replace the Indian soft coke industry wholesale by a large-scale low temperature carbonisation industry should be regarded with the greatest caution and circumspection until it is certain that these low grade coals are not going to be ousted from the market In the opinion of the author the desire to recover distillation products should not be allowed to cloud the main issue, which is that India has millions of tons of low grade but quite useful coals whose conversion into a domestic fuel and whose utilisation in other directions must be encouraged, not only for the sake of those members of the mining industry whose living depends on it but also in the interests of the conservation of our fuel resources

Now a large proportion of such low grade coals in India cannot be economically treated in a washery or other coal-cleaning plant Visual X-ray examination of the lump coal conclusively proves this Some of it, in fact quite a large proportion of it, does not, after crushing, coke so satisfactorily as the crushed coal or slack of the better seams, so that ultimate utilisation of this low grade coal in a modern coke plant does not necessarily (in the light of our present knowledge) offer any special attractions The present system of coking large lumps has obvious advantages—the preparation prior to coking costs nothing and the product is in lump form and travels well by road and rail without undue loss by crushing and production of fines

We may take it, therefore, that the present system of coking large lumps by a simple distillation process is likely, for some time yet, to remain as a feature of the coal industry, even though economically sound means may yet be found to recover part, if not all, of the volatile products, whose value as 'by-products' is, it is to be feared, somewhat over-estimated just at present And that statement does not negative any proposal to establish a modern low temperature carbonisation industry, using either the same low grade coals or those of better grade

It follows from the preceding remarks that the quality of the coals used for making soft coke is at present undoubtedly low Ash contents of selected lumps taken at random have been found to vary from as little as 8 per cent to as much as 38 per cent, but both these extremes are unusual and a more normal range is from about 12 to about 25 per cent, with an average nearer 16 or 17 per cent Such coals will, on distillation, yield cokes of correspondingly high ash content For example, a typical coal, such as is used, containing say 16% of ash will, on coking under normal high temperature conditions (*i e* at about 950°C), yield a coke containing as much as 21% of ash, and as the temperature in a soft coke heap is not anywhere near that temperature but closer to 400°C , less volatile matter is likely to be driven off, there is a slightly larger production of coke and the ash content is, therefore, less and in fact likely to be about 19 per cent in the instance quoted The average ash content of a large range of No 1 soft cokes has been found to be about 22 per cent. It should be remembered, of course, that there are many qualities and grades of soft coke and that it is sometimes a difficult matter to correlate the designations of the various grades in different districts These grades are not necessarily grades in respect of quality only In one district the expression 'No. 1 Soft Coke' is applied to large lumps of the best quality No 2 soft coke is of inferior quality but quite saleable at lower prices But there is a grade known as No 1½ This consists of small size or rubble soft coke of good quality Its quality may be better than that of No 1 or not so good, *i e* its quality is not between those of Nos. 1 and 2 (Incidentally it may be remarked that there is a preference in towns for soft coke of the above 'No 1½' grade whereas country consumers prefer the large lump coke, No. 1 or No 2) It is inevitable that even quite large lumps of very inferior shaly coal get into the heaps and these may prove not to have coked at all well Such very low grade coal may emerge from the coking process as 'stony soft coke' and even this low grade material finds a sale, but as it is not so largely used for ordinary domestic consumption it is not dealt with in this note (Some concerns specialise in the manufacture of stony soft coke) In other districts these appellations are not necessarily applied to exactly the same respective types or qualities of soft coke On the whole, however, the above descriptions apply

Reference has been made above to the acceptability of gas coke as a smokeless domestic fuel The word 'smokeless' was emphasised, because such cokes, while being acceptable on the score of their relative smokelessness, are not necessarily completely satisfactory in other respects The difficulty of ignition has been referred to but another difficulty may arise, namely, that of providing a comparatively 'soft' fire for some kinds of cooking When making a domestic coke it is not necessarily always desirable to aim at producing a 'first class' article, so far as ash content is concerned, and it is the comparatively high ash content of soft coke that actually offers certain advantages over the better quality gas coke Soft coke manufacturers aim, so far as the domestic market is concerned, at replacing as far as possible cow dung and other natural and local forms of fuels commonly used for cooking Most of the fuels that it is desired to replace burn with a steady quiet flame or even merely glow, and within a short distance of the flame or glowing mass the temperature may not be excessively high This feature of these indigenous fuels renders them specially suitable for the preparation of a large range of Indian foodstuffs In fact a complaint that has occasionally been levelled against the use of the best soft cokes is that the fire is too hot (The same complaint has been reported against gas cokes)

It is here that consideration of high ash in a coal assumes an aspect different from the normal For many domestic purposes in India a moderately high amount of ash is actually an advantage, because in the course of time after the fire has been prepared the accumulation of ash aids in damping the fire down and in producing a moderately hot glowing mass rather than a bright red-hot mass resembling a miniature furnace. For example, when frying with *ghee* and for boiling milk a moderate heat is essential, whereas for cooking rice, although many hold that a moderate heat is preferable, considerations of time make a hot fire desirable. Even for cooking some *dals*, owing to the difficulty experienced in softening the grain right through to the centre, long continued boiling over a moderate fire is preferred On these grounds, it will be clear that a domestic coke for use in India need not be of good (low ash) quality and it may even with advantage contain quite a high percentage of ash.

Domestic smokeless fuel should be not merely comparatively smokeless but also free from an undue amount of substances likely to produce objectionable fumes in burning Some Indian cooking vessels are so constructed that the gases resulting from the combustion of the fuel can gain direct access to the food. It is obvious that there is a strong possibility of certain constituents becoming 'fixed' in the food and imparting to it an objectionable taste.

It is reassuring to be able to report, from the results of experiments carried out in the course of the investigations, that soft coke made with low sulphur Jharia coals (and nearly all Jharia coals have very little sulphur) has been proved to impart no flavour to any food cooked by it, other indigenous fuels have not all passed the test so satisfactorily.

FUEL RESEARCH

By N N CHATTERJEE [*]

In tracing the history regarding the discovery of coal in India we have to go back to 1774 during the time of Warren Hastings The Geological Survey of India was established some time later apparently with the object of developing the coal resources and other economic minerals The earliest reports of the Survey Department mostly dealt with the coalfields of the different parts of India With regard to the personnel of this department during those days it may be mentioned that there were officers with special qualifications in mining who were entrusted with the development of the coalfields [†] With the establishment of the Mines Department in 1902 the Geological Survey Department discontinued to maintain the mining experts and to develop their laboratory for systematic fuel and economic mineral research I may quote here the following lines from Holland's declaration [†] in 1907 'Whether, therefore we like it or not, the official geologist in this country is bound by the terms of his appointment to remember that, either directly or indirectly, his work should aim in the long run at *development* of our mineral resources' In my opinion however, the *proper development* of coal and other economic minerals has not been maintained By *proper development* I would include not only the discovery of the mineral property but also the carrying out of systematic researches for finding out the various uses to which they may be efficiently put so that the producers and consumers as well as those interested in trade and commerce might be properly educated in this respect The people of this country have remained ignorant about the utility of these economic minerals for want of knowledge in industrial application of them Even now we do not find the conditions very much changed or improved This lack of knowledge with regard to the proper utilisation of coal among the producers and consumers is due to the lack of serious attention to the problems of research both by the Government and the industry

In the early days of the Geological Survey Department it will be found that the start was made in maintaining the mining experts If that beginning had received continued nursing we would have possibly found today a well-organised fuel research station established in the laboratory of the G.S.I side by side with the mineral research laboratory to help the mineral industry as well as in solving various problems The results of such investigations could have been broadcast in cheap pamphlets amongst the industry and the interested public, thereby educating them in the matter of mineral development

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[†] See Fox, C. S.—Presidential Address to the Min. & Geol. Inst. (1936), pp. 27-29.

[Published August 22nd, 1940.

and utilisation But from a careful study of the reports published by the G S I we find that no systematic researches on industrial lines have been carried out either on coal or on other economic minerals In this connection reference may be made to the brisk activity of the U S Geological Survey and Bureau of Mines and the geological institutions of the U S S R who bring out, year after year, much useful information with regard to their country's economic minerals and broadcast them in cheap pamphlets which have a very wide circulation reaching every corner of their country Similar steps should be taken by the India Government in publishing useful information in cheap bulletins If the U S A and U S S R can bring out publications at such a low cost there is no reason why the India Government should not be able to issue even cheaper publications when labour is so cheap in India The question is well worth investigating by the relevant authorities

Though one hundred years have elapsed since the development of the Bengal coalfield, we are still debating the question of establishing a fuel research station We do not yet know how long it will be before the actual foundation of such a station takes place I hope by now that the Central and Provincial Governments have realised the necessity of establishing research stations to study especially such a basic material as coal

Something may be mentioned here about the improper and unscientific method of coal utilisation by the railways of India It is well known that on the recommendation of the Noyce Committee in 1925 the Indian Coal Grading Board was started In some measure at least, the grading of portions of seams is the cause of much of the waste that is going on If partial grading and working of seams is stopped it should conduce to the conservation of coal The ways in which the high class caking and chemical grade coals are used up by the railways are well known and have already received much publicity. It is not yet known what steps the Railway Board is going to take in the immediate future to give up this wasteful practice If they start to use low grade non-caking coals even now, the high grade caking coals and chemical grade coals will be saved for their legitimate use The low grade fuels could be utilised efficiently in the pulverised state and coal or coke would be made into gaseous fuel for steam generating purposes, etc. The railways should be able to modify the fire-place of locomotive boilers to use pulverised coal This step would lead to better utilisation of lower grade coals. Locomotives are already in use in other countries to burn pulverised coal.

Intensive researches should be started to find out the possibilities of burning different grades of coal in a powdered state, to convert low grade coals into gas at central gas-generating stations to supply gas to the different industries in the neighbouring places. Economic possibilities of starting carbonisation plants should be carefully studied and if such a plant can be installed the recovery of oil and other valuable by-products could be made and the ideal smokeless patent fuel could be obtained. This semi-coke will be far superior to the low grade soft coke that is produced and marketed nowadays. The possibility of obtaining liquid fuel by hydrogenation of coal, etc. should also receive due consideration by such a Research Board It is also well worth investigation if gasification of coal underground as practised in Soviet Russia will be feasible and practicable in India The rich volatiles of the high class Raniganj coals should be utilised for the manufacture of chemicals and steps should be taken to prevent these coals from being used in locomotives and other steam-raising plants when other grade coals will equally suit their purpose.

The method of soft coke manufacture needs immediate improvement and it is to be regretted that the Soft Coke Cess Committee has been unable to make any marked progress in this direction A simple method of heating in chamber ovens should be evolved with arrangements for the recovery of by-products Investigations in the economic possibility of starting such a plant should be taken up and, if necessary, small concerns should combine and amalgamate to install and work an economic unit plant to produce and supply semi-coke of uniform and better quality The Fuel Research Board could well utilise the cess fund at the disposal of the Soft Coke Cess Committee and the surplus fund lying with the Coal Grading Board These are some of the ways in which research work could be started for the guidance and benefit of the coal consumers. Research work, if carried out in a well-organised way, would have brought about marked improvement in coal utilisation long ago and the things would not have remained in such a helpless condition as we find them today It is a pity that the Government allowed this state of affairs to continue for such a long time

According to the recommendation of the Burrows Committee a separate fuel research station should be installed and that about half the cost should be obtained by levy of cess on the coal industry Now that the people of this country have begun to acquire the consciousness of proper mineral development and have awakened to the needs of industrial research and experiment stations to foster the basic industries in India, I think it will not be difficult for the Government to devise ways and means to establish a fuel research and mineral research station at an early date The entire cost of such an organisation should be borne by the Government and it is not at all desirable that the coal industry should be subjected to any further taxation To have a separate institution with separate whole-time staff would be an ideal thing no doubt for the country if it can afford to have it But this involves a very big scheme which will take time to evolve and put into effect.

Until a well-organised, independent and separate fuel research station is established in India, I think that well-planned research work could be started without delay in the various lines of coal investigation in the existing institutions for the immediate benefit and development of the country's resources. To give initiation to such a programme of work, I would suggest that the India Government be moved by the coal industry so that the various technical and research departments under the control of the Central Government may be asked to take up certain important and useful problems of coal research and that various other recognised laboratories in India may also be approached to undertake pieces of suitable work and co-operation and co-ordination should be maintained by a central organising body This programme, if carefully worked out and followed by such an organising Board, will give an early return at a minimum cost About the India Government departments mention may be made of the Geological Survey of India, Industrial Research Department, the Alipur Test House, Indian School of Mines, Cawnpore Technological Institute, etc Of the private bodies mention may be made of Messrs Tata & Co , Bird & Co , etc and of some of the well-equipped laboratories of Indian Universities If it is found that some of the Government departments have suitable workers and laboratory facilities, there should be no difficulty in persuading the Government to take an interest in the matter and to render help to the industry Moreover I believe that it is also the duty of the country's Government to see that various technical departments under its control carry on researches into some important economic problems relating to different industries and that results of such investigations are made widely available to the people There should be a central all-India body to control and supervise the work to be carried out in the different institutions and to co-ordinate the results obtained from these different sources Such a body may be styled as the National Research Council The National Institute of Sciences of India may be given the power to form expert committees in connection with various branches such as Fuel Research Board, Agriculture Research Board, Chemical Industries Research Board, Metallurgical Research Board, etc These boards will distribute work among the different laboratories and supervise the work whenever necessary Salaried research assistants and scholars (both whole-time and part-time) may be appointed to work under the guidance of competent authorities Regarding the equipment of the laboratories I would suggest that the laboratories themselves should give partial financial help in necessary equipment as this type of research when conducted in those laboratories will materially help the teachers and students alike In this way definite and well-planned work may be immediately started through the co-operation of the different laboratories. In this connection reference may be made to the excellent work carried out by the various engineering and experiment stations run by the United States Bureau of Mines in co-operation with some of the Universities as well as with certain local industries. In this way an immense amount of exceedingly useful work beneficial to industries has been accomplished in the U S.A.

If this scheme is favoured, a conference of representatives of Government research departments and those of willing private firms and Universities may be held when the distribution and allocation of work in different lines of coal research may be discussed and arrangements made for meeting the expenditure in connection with the officers of the central board, laboratory equipment, research assistants, scholars, etc.

The scheme as outlined above in skeleton will require only a fraction of the heavy capital expenditure of establishing a separate and independent research station and this scheme can be made to work in a short time

If the National Institute of Sciences of India is given the responsibility and status of that of the National Research Council of other countries I think it will prepare a scheme for work in the lines suggested above in the best interests of the country and will surely prove itself worthy of its name.

It should be mentioned here that simultaneously with the initiation of fuel research there should also be research on safety in mines, *i e* for the safety of labourers and for the safe and maximum extraction of coal It is time that India began to solve her problems in relation to the local conditions and needs instead of being idle or borrowing ideas from others There is talent enough in the country which could be employed to useful purposes. It is for the Government to organise the work and utilise this talent for the ultimate good of the country.

FUEL RESEARCH IN INDIA

By C FORRESTER, *A H W C , F I C , Ph D , F R S E , Fellow of the Institute of Fuel*

This is a subject on which much has been written in recent years, even in India, and it is probably hardly necessary, except for the sake of ensuring a proper assessment of the position, to recapitulate the arguments that support the demand for research into the better utilisation of fuel, and particularly of coal Many scientists and practical mining men also have in recent years stressed the importance of India following the example of almost all other civilised countries and establishing some sort of organisation for this purpose. Messrs W H Phillips (1911), E H Pascoe (1924), C S Fox (1924, and in many papers since), J Coggin Brown (1927), H K Sen (1927), J Thomas (1930), C H McCale (1930), N P Gandhi (1930), N N Chatterjee (1930), D Penman (1932), the author and a host of other workers in this field have, in published papers and in official communications, fully expressed their views on this matter so fundamentally affecting the future prosperity of the mineral industry in general and the iron and steel industry in particular

What is more important is that so many other countries that have, till recently, regarded fuel research as something to be sponsored by wealthy Governments only, have realised that research is the life-blood of modern industry Mention need be made only of the research work of the Canadian Bureau of Mines, of the New Zealand Bureau of Mines, and the Fuel Research Institute of South Africa, as well as of similar organisations in China, Japan and the U S S R., to give point to the remark South Africa's recent action in establishing a Fuel Research Institute by utilising the funds collected by the formerly-existing Coal Grading Board is peculiarly interesting to us in India, especially as Africa's coal problems so closely resemble ours, as do her financial problems

Let us assume, then, that the establishment of properly organised fuel research must come in this country and examine the problems waiting for us to deal with.

Much attention has been publicly focussed on the pressing problem of conservation of our coal resources and the recently-issued Report of the Coal Mining Committee has brought the whole subject to the front. In their recommendations the Committee have suggested the establishment of a 'Coal Research Board' but have left its functions undefined 'Coal' research may mean safety in mines research, which aids in effecting conservation, or fuel research which, by making utilisation more efficient, more directly aids in effecting conservation. One of the problems that has been more stressed than any other in public discussions of this subject has, of course, been the

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conservation of the country's reserves of coking coal The whole future of the industrial life of India is bound up with the future of these reserves and obviously it is only proper that we should do anything that can be done to reserve for their 'proper' use those coals at present used for other purposes than those for which they are best suited But there are many other problems, some of them equally important, others of apparently minor importance but none the less essential in the part that their investigation may yet play in the proper utilisation of India's coals

The following list is extracted from a Memorandum prepared in 1934 by the author and submitted to the Government of India in support of a proposal to establish a Fuel Research Department in India —

1. Systematic physical and chemical survey of the coals of the various coalfields in India with special reference to—
    (*a*) specific gravity as related to ash content,
    (*b*) proximate analysis (by proper standard methods),
    (*c*) coking power,
    (*d*) chemical analysis of ash,
    (*e*) ultimate analysis,
    (*f*) fusibility of ash and tendency to clinker,
    (*g*) separation of banded constituents and other rational analysis
2 Nature and amount of volatile matter expelled from coals at various temperatures, with special reference to manufacture of good quality soft coke for domestic purposes
3. Laboratory- and medium-scale investigations on washability of second grade and low grade coals and of slack coal
4 Visual investigation of nature and distribution of mineral matter in . coal by X-ray examination (This refers to incombustible mineral matter)
5 Large-scale briquetting tests, especially with a view to investigate the possibilities of briquetting without the use of a binder
6 Investigation into the causes of spontaneous combustion of coals in Indian coal mines.
7 Conversion of Indian coals into oil.
8 Extension of the use of Indian coals in gas producers
9 Valuation of Indian coals with a view to encourage purchase and sale to specification and on analysis

To the above may be added others to which reference is made below. The following comments upon the above are offered as a stimulus to discussion on the question and with a view to elicit the opinions of others as to the relative importance of those various suggested lines of research and our ability to prosecute them in India in the most efficient manner possible.

1 *Systematic survey of the coals of India*

This has, of course, been already done geologically and, by reference to existing analytical information, chemically but it has not been done systematically in reference to sub-heads (*a*) to (*g*) The Department of Scientific and Industrial Research of Great Britain has for the past few years been engaged, through the Fuel Research Board and the associated universities and colleges, on a wholesale survey of this nature and already the results have proved to be of great practical value to industry Apart from the scientific value of such a comprehensive survey, the practical value of the knowledge gained by accurate and standard methods of investigation cannot be overrated, especially in these days when so much in India depends upon export trade Special reference might be made to the great interest recently taken, by overseas buyers of Indian coal, in the chemical composition of the ash and its fusibility, with reference to possible clinker trouble The amount of information regarding fusibility is somewhat meagre and it is to be feared that much of the equipment available in the country for this work is not designed to give accurate information comparable with that supplied by standardised apparatus used, say in Britain or America As for the chemical composition of Indian ashes we are in almost as bad a position A few analyses of Indian coal ashes are quoted in the publications of the Geological Survey of India and special mention may perhaps be made of the most recent contribution by Mazumdar given before the last session of the Indian Science Congress and published in full in the August 1938 issue of 'Fuel in Science and Practice'. The industry badly wants much more of this work to be done and a determination of fusibilities of the same ashes, in both oxidising and reducing atmospheres is equally desirable

A similar investigation into the fusibilities of ashes of mixed coals is of equal importance owing to the failure on the part of both suppliers and consumers to realise that mixing coals entails grave risk of clinker trouble due to the almost certain lower temperature of fusion of the mixed ash

A branch of this work that is of great importance both from the purely academic point of view and for the purpose of classification and correlation of coals is 1(*e*), ultimate analysis Especially in respect of the determination of the amount of oxygen in Indian coals we are sadly deficient in information about their composition The determination of oxygen in a coal is an extremely difficult one that only most experienced fuel technologists can with confidence undertake and bound up with it is the careful analysis of the ash, with a view to develop a formula for Indian coals corresponding to Parr's Formula, in order to calculate the amount of mineral matter in coals from a study of the amount, and chemical nature, of the ashes. The practical benefits of Seyler's classical work on classification of coals cannot become available to us in India until this work is undertaken and carried to a successful conclusion.

2 *Volatile matter and carbonisation at different temperatures.*

On this important subject, also, little has been done The Indian Soft Coke Cess Committee has had some work done and a large series of Jharia-Barakar coals has been investigated by the author with reference to distillation products obtained at temperatures varying from 300° up to 950°C Some of these results have been utilised in aiding the further investigations, but none of them has yet been published in detail (a defect that it is hoped will be remedied shortly) Prof Roy, President of the Geology Section of the last session of the Indian Science Congress (Lahore, 1939), quotes the results of some similar distillation experiments carried out by workers at Calcutta University Apart from these figures it is doubtful whether any systematic work has been done In these days when improvements in methods for manufacturing soft coke, and low temperature distillation processes, are much in the public eye, it is highly desirable that the work done so far should be supplemented without delay

3 *Washability of coals*

The only work known to have been done in India on this subject has been by (*a*) Randall in 1924, and (*b*) Forrester in 1936 The former was limited to a few experiments using a froth flotation experimental plant and without constructing fully informative washability curves, and the latter was confined to an examination of coals known already to be comparatively clean and free from stone bands, though complete washability curves were constructed from the laboratory work

Although the latter dealt with Jharia coals (and that work has been published) and with a selection of Raniganj coals (the results of which have not yet been published) only the fringe of the subject has been touched An extensive washability survey of run-of-mine coal and 'whole of the seam' coal is highly desirable The industry cannot at present be said to know what possibilities there are in the cleaning of coal in India

4 *X-ray visual examination of coals*

This work is an adjunct of the preceding, *i e* washability, and need not be enlarged upon here except to explain that it ought not to be confused with the more academic matter of examination of the internal molecular or crystal structure by means of X-rays.

5 *Briquetting*

The importance and various aspects of briquetting have been dealt with by the author in a separate contribution to the *Symposium* and will not be dealt with here.

6. *Causes of spontaneous combustion.*

This subject has engaged the serious attention of the Department of Mines for several years now and would in all probability be considered to be within the scope of a Safety in Mines Research Department, and the subject of safety in mines is dealt with in a separate contribution It is worth while pointing out, however, that the results of some of the work of a Fuel Research Department would undoubtedly tend to throw much light on this important problem, so vitally affecting the industry at the present time

7 *Conversion of coal into oil*

This is a subject on which information regarding Indian coals is undoubtedly required But the author is inclined to the view that work on this problem can very well be delayed until we have more information regarding the progress in other countries, as comparatively simple tests, indicating the 'rank' of the different coals, can give almost all the information wanted with reference to any particular coal A comprehensive laboratory study of a large range of coals with reference to this subject seems, to the author, scarcely to be justified at the present stage Other workers, however, may not be in agreement with this view

8 *Use of coals in gas producers.*

It is questionable whether any completely separate series of investigations into this subject is really necessary But information regarding Indian coals is required to judge the suitability for their extended use in gas producers, and the information would be obtained from the results of 1(*b*), 1(*c*) and 1(*f*) above

9 *Purchase and sale to specification and on analysis*

This is partly within the scope of the economist but the scientific investigator should interest himself in the devising of suitable practical formulae likely to be acceptable to various industries with a view to extend the adoption of more rational methods of valuing coals. The author realises that the extended adoption of the specification system would ultimately tend to dispense with the present grading method but the industry would benefit ultimately, and the cause of conservation would be immeasurably advanced

One major problem likely to be a fruitful subject of research is that of *blending of coals* with a view to use a greater proportion of non-coking or weakly-coking coals for coking purposes, as well as to lessen the trouble sometimes experienced with coals of high swelling power that, on account of insufficient subsequent contraction in the coking process, cause serious deformation and ramming trouble in coke ovens This is also a subject that could better be done in the country and should be undertaken with little delay

Full-scale experimental work has been carried out on this subject in India by Lathbury and Marshall in 1919 and by Lancaster and Marshall in 1927. In their experiments Lathbury and Marshall tried the effects of mixing different proportions of good quality Giridih coking coal and upper Raniganj non-coking (or not good coking) coals, and Lancaster and Marshall included in the scope of their later work poor coking coals from the *lower* Raniganj measures as well as from the Bokaro and Karanpura fields [A full report of the results of both series of experiments is given by Fox in *Rec G S I*, LXI, 1928-29, 294–314]

The results of these experiments conclusively show that there is scope for further investigations, both in the laboratory (using the various types of apparatus for testing swelling and contraction) and on a large scale by coke oven tests

The foregoing remarks apply chiefly to research on the preparation and utilisation of coal India possesses vast *additional sources of power, both actual and potential*, for example, wood and other vegetable substances and the various substances that can be obtained from them either by distillation or by fermentation Special reference may be made to the work of various investigators at the Indian Institute of Science in the direction of hydrolysis of waste carbohydrates such as rice straw by dilute sulphuric acid, followed by fermentation of the sugar produced The treatment of other waste substances (including such pests as the water hyacinth) has also been suggested and much sporadic experimental work has been done There are in India countless hundreds of similar potential sources of alcohol that may yet be profitably investigated

The author would also point to the great possibilities of the more extensive use of wood and wood charcoal (especially the latter) as the source of producer gas for gas-driven internal combustion engines, *i e* motor cars driven without petrol The wood-gas motor car is now a practical proposition India, with the problems of vast distances and the accompanied problem of high railway freights, might well utilise her otherwise useless woods (*i e.* useless as timber) more efficiently as a source of fuel

The spade work on *hydrolysis and fermentation has already been done for us* All that is required is to apply the well-known facts to the raw materials available. Here is another wide field of investigation for the research worker

How, then, is this great programme of research work to be accomplished? The question has been asked over and over again, in public meetings, at annual dinners of scientific societies, in informal discussions among mining men and their more academically scientific friends, and the answer seems never to be forthcoming The coal industry, when it has shown signs of interest in the subject, has maintained that it is the affair of Government Government, when challenged on the matter, have said that the industry should first make a move. The result is stalemate, except that individual workers, both among the important coal mining companies and among individual scientific workers in technical colleges and universities as well as, of course, the staff of the Geological Survey of India, have materially contributed to our knowledge of the composition and properties of our coals

The trouble is that the work has not been carried out in a systematic manner. There has, naturally, been no systematic co-operation or planning in the work so far, *i.e* co-operation between different workers and, as stated elsewhere ('Methods of Analysis of Coal in India' in this *Symposium*), much of the published work—perhaps as much as 90% of it—has been done by methods that render it almost certain that it will have to be done over again

The remedy is, in the opinion of the author, *either* to establish a non-official all-India scheme of co-operation between fuel technologists and other workers in the field, with a voluntary (and voluntarily accepted) central distributing bureau for co-ordinating the work of the various persons taking part in the scheme and for distributing systematically samples of the various coals that would be examined, so as to avoid overlapping and the loss of valuable relative information about the same coals from different sources, *or* to induce the Government of India to establish, as soon as funds permit, a central Fuel Research Station

On the assumption that it would be possible, as it is found possible in Britain, to obtain the co-operation of workers in technical colleges and universities (as well as of trade organisations if formed) the second alternative appears to the author to be preferable

The requirements of the industries likely to benefit from this work cannot be adequately met by the results of work carried out solely in universities and colleges, the staffs of which have other onerous and distracting duties to perform If the work has to be of first-class quality and if much overlapping and unsystematic work has not to be undertaken, a full-time central controlling authority must ultimately be appointed The expense may in the beginning be just what we care to limit it to, provided, of course, that a reasonable minimum is conceded, and the work that can be undertaken would depend almost directly upon the amount of funds available

The apparatus and equipment required for most of the subjects suggested is not unduly costly Much of it could be made immediately available from various sources until such time as the indications of the results likely to be achieved justified permanent establishment of the central station If a purely organising and administrative central authority were established, seeking co-operation, and helping in the direction of the work, and of course, financing the publication of the results, a total annual expenditure of under Rs.50,000 per year would probably be ample If a centre were to be established in or near one of the coalfields for a central laboratory and library, still working in co-operation with other laboratories throughout India by a distribution of work in which different workers were interested, an initial expenditure of about Rs.25,000, with an annual recurring expenditure of about Rs 50,000, would be sufficient. When it is remembered that the magical figure of 'a lakh of rupees' is merely about £8,000 the corresponding figure of over £80,000 spent by the British Government on the Fuel Research Board, as well as the large sums separately spent by various coal trade organisations on research work, make our present proposals acquire considerable merit on the grounds of modesty.

The views of the various universities, technical colleges, Government departments, and individual workers on the possibilities of co-operation might well be invited, in order to enable the Government of India to judge to what extent the institution of a central organisation would be feasible

In the meantime the most urgent need, in the opinion of the author, is a reliable central research bureau, kept up to date by an efficient fuel technologist with the help of first-class clerical staff As the years go on the amount of valuable information that is accumulating is increasing and it is daily becoming more and more difficult to ensure that one has access to all the important literature on any one subject (This is a problem not exclusively that of the fuel technologist) Such a central bureau can be established at little expense But if it is established it must be comprehensive and complete No half measures are worth the trouble expended on them.

FUEL RESEARCH INDIAN COAL

By CYRIL S FOX, *D Sc*, *M I Min E*, *Geological Survey of India*

A complete research on all aspects of Indian coal would involve an immense task which would probably have to be carried out under three main divisions —

(1) Dealing with geological occurrence of the coal and including a study of the coal seams and the chemical constitution of the coal,

(2) Dealing with the mining of the coal, questions of heating, fire-fighting, dust explosions, packing and general questions of drainage and ventilation, and

(3) Dealing with the utilisation of the coal including problems of cleaning, coke making, pulverisation, gasification and hydrogenation as well as storage

This would be impractical in India at present and several of the questions are not yet in need of immediate attention Of the 28 million tons of coal produced last year only a relatively small proportion is used as a raw material in gas works, preparing metallurgical coke and soft coke—possibly not 7 million tons in all or 25 per cent as against the remaining 21 million tons which is used as fuel for steam raising, etc

In my opinion an Indian Fuel Research Board while co-operating with existing organisations should concentrate on a few problems which when satisfactorily solved would provide data of commercial value To mention only one such problem I would refer to the large quantities of low-ash high-moisture coals which are liable to spontaneous combustion in storage or ships' bunkers and are thus unexportable

Returning again to the main divisions of research and the possibilities of co-operation it can be said at once that the

(1) geological questions can best be left to the Geological Survey of India who have already surveyed most of the coalfields in this country but who do not possess the facilities nor the staff for making a chemical survey of the seams,

(2) chemical study of the coal seams, bed by bed, traced throughout a coalfield is best carried out by the chemical departments of provincial universities or schools of mines working in touch with the Geological Survey and the Fuel Research Board

Thus chemical study may include numerous questions.—

(*a*) study peculiarities of different coal seams, as traced from locality to locality,

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(*b*) assist in bringing the chemical and physical data into line with the geological information,

(*c*) investigate different methods of coal sampling in the mines, for boiler trials and for export,

(*d*) suggest uses for coals whose peculiarities have been proved,

(*e*) publish information on the analyses and studies which have been made

(3) With regard to the purely mining problems such as ventilation, underground fires, coal dust, explosions, underground drainage, subsidence due to de-pillaring or collapse, etc it would seem best to have these investigations made by committees appointed by the coal associations, mining institutes and such bodies in close touch with colliery companies and the mines These are matters which get very close to the pockets of those engaged in winning and marketing coal and they would have a close personal interest in the investigations by establishing a colliery owners' research organisation.

(4) Finally, there is the subject of the utilisation of coal and the various possibilities for cleaning coal, preparation of soft coke, improvements in hard coke manufacture, the recovery of gases and liquid fuels, the hydrogenation of tars, the testing of inventions or processes, investigation on pulverised fuel firing, the slagging of coal ash, and related questions. There is little doubt that as these investigations are of direct practical value they should be conducted by the special staff of the Fuel Research Board itself absolutely independent of any other department, association or educational institution. The chief objective of this central section of the Fuel Research Board is to try out processes, make tests, prove equipment and generally function as an experimental institution to prove and draw attention to various ways of using coal more economically, safely and profitably

SAFETY IN MINES THROUGH EDUCATION

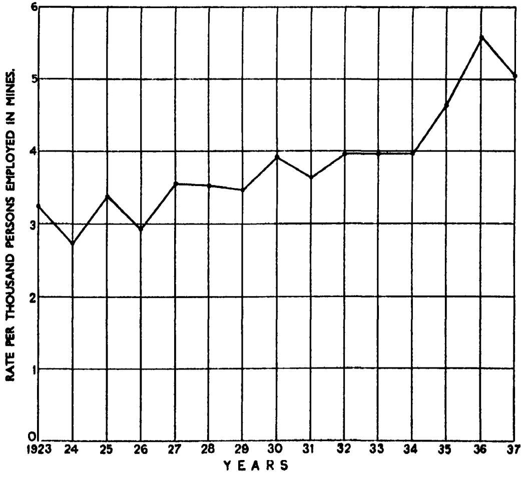
By H K NAG, *M I Min E*

Coal Mining in India for commercial purposes dates back to 1774, but due to transport difficulties no serious attempt could be made till the opening of the East Indian Railway as far as Raniganj in 1855

At the time, the output was mainly derived from open workings and the annual quantity was even less than 100,000 tons Attention to the safety of the workmen was unnecessary and was hardly thought of

Proper measures for safety were officially introduced by the Government of India in 1901 by the promulgation of the Indian Mines Act including Rules and Regulations based on the British Mines Regulations

The mines were then shallow and the total annual output was 6 6 million tons Along with the gradual development of the industry and as necessity



SERIOUS INJURIES (INCLUDING DEATHS) PER 1,000 PERSONS EMPLOYED.

TEXT-FIG. 1.

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arose, further legislation continued to be introduced and enforced and probably the limit of legislation has now been reached

It is well known that Indian Mines, in which a number of thick seams occur in close proximity to one another, present enormous difficulties and the danger of mining increases considerably with the depth and intensity of mechanisation

The danger is all the greater during the de-pillaring operations in 'Bord and Pillar' work—the common method practised in India—and it might be pointed out here that more than half of the present output is being obtained from such de-pillaring work

From calculations based on information collected from the Reports of the Chief Inspector of Mines, as shown in the graph (Figure 1), we find that at all mines under the Indian Mines Act, the rate of serious injuries, inclusive of the number of lives lost per thousand persons employed, is gradually increasing Even if we eliminate the figures of 1935 and 1936, which might be considered unusual, the position does not show an improvement

It should, however, be mentioned here that the death rate per thousand persons employed in coal mines continues to be satisfactory, the average being 1·31 for the preceding 15 years up to 1937, as compared with 1·06 of Great Britain for the equivalent period ending 1936

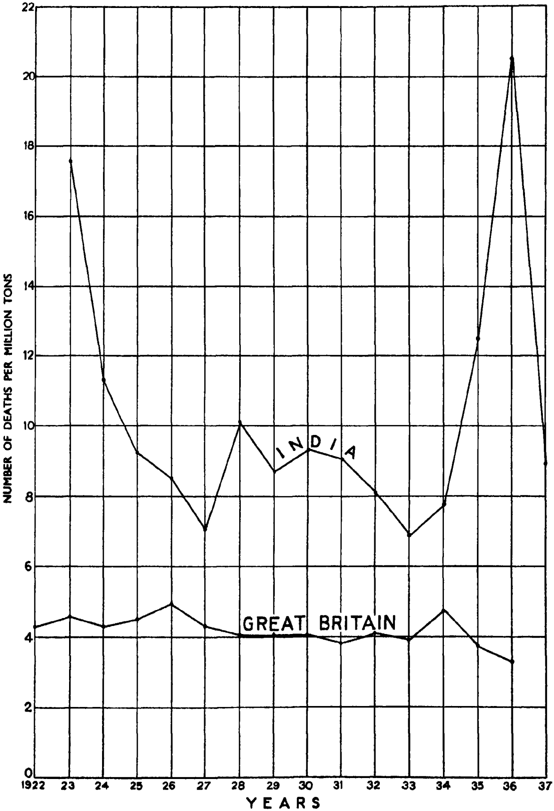
The classification given below affords us data for the examination of the causes of the fatal accidents taken over an average of the preceding 15 years.

	Per cent
(*a*) Misadventure	64·04
(*b*) Fault of the deceased	18·04
(*c*) Fault of fellow workmen	4·30
(*d*) Fault of the subordinate officials	7·36
(*e*) Fault of the management	5·62
(*f*) Faulty material	0·74

Figure 2 illustrates the Indian position regarding the death rate per million tons raised at coal mines in comparison with that of Great Britain It will be observed that this death rate in India is more than double that of Great Britain and also that of America where the rate is more or less equal to that of Great Britain

From a careful study of the above chart and the classification of the causes, we find that the death rate due to the fault of the deceased, fault of fellow workmen and misadventure and also the death rate per million tons of coal raised could be greatly improved if the labour available for the mining industry were of better quality.

The position now is that everything has been done which is possible by legislation, through the best efforts of the Mines Department in co-operation with the management of mines. There seems to be hardly any room for



NUMBER OF DEATHS PER MILLION TONS OF COAL RAISED.

TEXT-FIG. 2.

the introduction of any further regulations which might improve matters in this direction.

Since the early years of the present century the Government of India had under consideration the question of devising means of reducing large avoidable waste of coal, of improving the methods of extraction, and of affording greater protection to life and property In 1919, this resulted in Mr Treharne Ree's report on methods of mining which was followed by the report of the Coal Fields Committee of 1920 and lately the report of the Coal Mining Committee in 1937

The main recommendation in these reports relates to the filling of the voids made during the recovery of the coal by incombustible stowing material —commonly known as Sand Stowing

This method, although expensive, if and when introduced, will undoubtedly go a great way to minimise the danger to life and property

The Government of India have already started taking action in this respect, and I, therefore, at the moment, feel that there is no necessity to deal further with this aspect of the question.

Now let us examine the type of labour we get in our coal mines

The Indian mining labour was primarily agriculturist who took to mining as a secondary occupation Comparatively higher earnings have tempted some of them seriously to take up mining work as their profession, but still quite a large proportion of the labour periodically disappears from the mines to return to their villages for the purpose of cultivation Practically the whole of such labour force is illiterate, ignorant, non-ambitious and inefficient and unable to realise the necessity of obeying or observing the Mining Regulations

It is our common experience to see them congregating below ground in dangerous places, often deranging ventilating arrangements, etc , neither do they consider it illegitimate to rob coal from the pillars or to enter prohibited or fenced off areas in order to get easy coal Their ignorance is sometimes colossal and the writer has personal experience of a miner piercing the top of his safety-lamp in order to improve the illumination. Fortunately in this case there was no gas present, otherwise the result could better be guessed than imagined

The problem of labour in the coalfields, therefore, is a most difficult one, as the quality is nowhere near the requirements of the industry The labour should be healthy, efficient, disciplined and trained with a sense of safety With such qualities, the output per man can be considerably increased, thus reducing the death rate to a minimum in relation to the tonnage of production of the mineral A good and efficient labourer not only improves his own wage-earning capacity and status, but is also less of a danger to himself and to others, and is more of an asset to his employer

The introduction of sand stowing, further safety legislation, the formation of rescue stations and brigades or the appointment of safety officers, etc.

cannot, however, result in the maximum benefit, unless the workmen concerned are capable of understanding the dangers associated with modern mining and are made sufficiently alert and alive to such dangers and know how to avoid or to combat them Mere legislation in the Statute Book cannot produce results unless the people concerned are educated enough to observe and benefit by it. It is, therefore, very necessary that urgent and immediate attention should be paid for their suitable education, which has so far been sadly neglected both by the owners and the Government, though much has already been and is being done to improve the housing, sanitation, water-supply, medical help and general welfare of the labour

Considerable attention has been paid in recent years to the education of the Supervisory Staff and of Mining Engineers The Indian School of Mines, the Provincial Evening Mining Classes and the Benares Hindu University are already supplying trained Surveyors and Mining Engineers The Provincial Governments and the State Railways have established classes at suitable centres in the coalfields for the training of Overmen, Sirdars and other supervisory staff There is thus fairly adequate provision for the management and supervision of mines but the same cannot be said in regard to the labour force

The urgency of the question of the education of the labour force was felt long ago and although it was known to all of us that the accident rate amongst this class was highest, no serious attempt was made in this direction. Even this very important aspect escaped the attention of the Royal Commission on Labour who visited the coalfields in 1930.

There are a few primary schools in the coalfields established by the Colliery Owners for the education of miners' children But the number is far too inadequate to be of any use In 1930, the Bengal Rural Primary Education Bill was passed as Bengal Act VII of 1930, under which Act a cess was to be levied on the Mines and Quarries for the introduction of primary education. In practice, however, nothing has been done

Adult education, if anything, is in a still worse state. The approximate number of adult labour in coal mines is in the region of 180,000. The cost of educating them should not be prohibitive and the benefits derived will more than justify the expense. It is not suggested to give the adults fairly extensive primary education, but a start should be made in giving them the necessary safety education through films and lantern slides accompanied by lectures and demonstrations, etc, that is to say, by combining recreation with enlightenment, more or less on the same lines as was followed successfully in the United States of America in educating the Negro mining population.

Regarding the labourers' children, compulsory elementary education, with syllabuses made to cover practical instruction in mining and its dangers, should immediately be introduced. The expense of such education should be shared by Coal Owners and the Provincial Governments alike.

The above course is a suggestion for the consideration of all concerned and a proper committee should be immediately established to go into the question thoroughly and draw up a comprehensive and workable scheme

It is gratifying to mention here that the ministry of Bihar has recently taken up the question of adult education all over the province including the mining areas The District Officers and the Educational Authorities of the province have, it is learnt, enthusiastically taken up the work and Local Committees have been established to impart elementary education to the adults within these areas

In the modern campaign for greater safety in coal mines as practised in other parts of the world, one of the principal items is education of mining labour In India this has been entirely lost sight of, and it is time we devote serious attention to this problem I would, therefore, conclude by appealing to the Colliery Owners, Labour Organisations and Governments (both provincial and central) to give their immediate consideration to so important a matter and thereby help to increase the efficiency of the labour as well as reduce the accident rate in our mines.

SAFETY IN COAL MINING

By E B PARK *

General

The first thought that occurs to one on reading the title of this paper is that 'Safety in Mines' is only a relative term, there is not now safety in coal mining and there never has been, coal mining has always been a dangerous occupation and in spite of the vast expenditure in brains and money on the subject of increasing the safety in mines the dangers still remain, I think, as great as ever This is not because the brains and money spent on research have been wasted, but because as mining proceeds to greater depths conditions of work become more difficult and dangerous, and also the trend of modern requirements for intensive mining, with its concentration of men and machinery in small areas for large outputs, raises problems which were very much less noticeable under the more leisurely old-fashioned methods of working.

Method of dealing with the subject

The heading safety in mines embraces a great number of practical and scientific factors relating to various phases of the working of a colliery and I propose to discuss the matter briefly as it affects the different phases of the work

Safety in shafts and on haulage roads.

Accidents in shafts are, fortunately, extremely rare except in the case of the actual sinking of the shafts, I say fortunately because the thought of an accident in the middle of a deep shaft, in say England, where as many as 100 men may be in the two shaft cages at one time, simply appals the imagination The reason for this lack of accidents is that the only things that can go wrong are the winding engine, winding and guide ropes and accessories and the cages themselves, all these are governed by very strict regulations as to length of life, inspections, etc , and as in addition everything is easily accessible for inspection there is consequently very little tendency for the inspection to be neglected

Accidents on haulage roads, on the contrary, are distressing by their frequency, and in spite of the stringent regulations enacted in all countries a glance at the annual report of the Chief Inspector of Mines of any country will show that accidents on haulage roads form a large proportion of the total number of accidents

The reason for this is to my mind two-fold firstly, the haulages are underground and very often stretch for long distances in-bye so that thorough inspection of track, signalling apparatus, safety appliances, etc is a job which calls for extreme efficiency on the part of the subordinate staff concerned, secondly, it is the old tale of 'familiarity breeds contempt', the men working on the haulages are doing the same job day after day and unless the management are extremely strict in enforcing the rules relating to working of the haulages slackness sets in and the men start taking risks until an accident occurs

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* Loyabad Colliery, Manbhum.

Every mining man knows the rules the application of which will reduce his haulage accidents to a minimum, but it may not be out of place here to jot down a few of the most important —

Manholes must be provided as required by the Act, must be of proper size and kept clean

No person must be allowed to travel or work on the haulage road while the rope is in motion unless specially authorised to do so

No person must ride on any set of tubs unless specially authorised to do so

The signalling apparatus and the track must be kept in first class order throughout the length of the haulage road

Stop blocks must be placed at the top of every brow or incline and must be kept shut.

On a main rope haulage from the dip a drag must be attached to each ascending set of tubs.

On an endless haulage on a gradient automatic jack catches must be placed at intervals to prevent the tubs from running back if they become detached from the rope

Where men are working on a haulage road in the dip and the haulage is working above, good buffers, preferably in the shape of stout steel derrick props, must be provided.

No men must be allowed to stand or sit on the junctions where side roads join haulage roads

Haulage engines, ropes, caples, tub links and tub drawbars must be examined regularly

Accidents due to falls of roofs or sides.

This class of accident again is one which contributes a big percentage of the total number of accidents in mines and unfortunately it is extremely difficult, if not impossible, even to form rules which will eliminate it.

The danger from falls of roof and side is one which is inherent in mining and it is really only the practical mining knowledge of the average workmen in the mine which can keep it at bay; when a man has worked down a mine for several years he develops a sixth sense which tells him when a place is safe and when it is not, if he does not develop this sense he is booked for the casualty list, it is a result of hard practical experience and no amount of book learning will give it to a man although it is true of course that a man with his brains sharpened by a good education will pick it up more quickly than one who has not been so fortunate.

As with haulage accidents, so with falls of roof and sides, it is often over-confidence or slackness on the part of the men concerned that causes an accident They know that, for example, another prop should be set before they cut any more coal but perhaps they only need a few more basketfuls to complete a tub, they risk it and take the consequences

The only safeguard against accident of this type is a very strict insistence on safe timbering and work in general by the management and subordinate officials so that a man knows that if he deliberately runs a risk he not only risks his life, but, if he gets away with it, he will still be in trouble with the management

It is only fair however also to show the other side of the picture which is that in many cases, especially in de-pillaring work in this country in thick seams of 20′-0″ or more thickness, the conditions of work are definitely dangerous and it is a wonder to many of us who have to supervise the work under these conditions that accidents are not more numerous than they are; it says a lot for the skill of the average miner at his own particular job

Accidents from shot-firing

The rules laid down by the Mines Act and Regulations in this country, and in most other countries as well, with regard to shot-firing in mines are very strict and it is largely owing to these rules that the accidents directly attributable to shot-firing are not actually very numerous, there is always a grave potential danger from men overcharging shot holes, firing shots without warning other workmen in the vicinity that they are going to do so, or firing shots when there is any CH_4 present in the neighbourhood of the place where the shot is to be fired, but all these cases are clearly covered by the regulations under the Mines Act and these regulations are strictly enforced in any well-managed colliery.

The greatest danger from shot-firing undoubtedly is the ignition of gas or coal dust which may lead to an explosion, but the compulsory use of 'Permitted' explosives in gassy mines and the compulsory use of inert stone-dust have reduced these dangers to a minimum

Another cause of danger from shot-firing is the mis-fired shot, the fuse of a shot is ignited or the electrical exploder is worked and the shot does not explode and there is a dangerous tendency for the man concerned just to wait about a minute and then go in and see why nothing has happened, as it is not an infrequent occurrence for the explosive to have a delayed action for some reason or other anyone doing this is running a very grave risk, and the Mines Act lays down that if a shot is mis-fired the place must be fenced off by an official and no one may go near for at least an hour, and then they may not try to examine the shot-hole or pull out the explosive but must bore another hole, fire it and then search for the unexploded charge which must be accounted for

If the regulations are adhered to in these cases there is very little danger

Accidents due to machinery

Accidents due to this cause in mines may be either on the surface or underground, on the surface they are of course no more likely to occur than in any workshop or factory, but underground there is the added difficulty that the lighting, even under the best conditions, is inferior to that on the surface, and in order to keep these accidents to a minimum it is absolutely essential that all underground machinery shall be really well fenced off and that no person shall be allowed to go inside the fencing while the machinery is in motion; another point which only applies to this country, but which is definitely most important, is that all machinery attendants and fitters must wear some kind of shorts and not dhoties which are extremely dangerous articles of apparel when there is moving machinery about

Accidents due to CO_2 and CO gas

These accidents are not common, but they do occur and they are usually due to ignorance on the part of the men concerned, or slackness on the part of the supervising staff.

It is of course essential that the officials of the mine shall be able to detect these two gases and if they find any of either gas the place must be fenced off, CO is only found when there is heating and as it is invariably accompanied by the characteristic gob stink the danger should be spotted and tackled at once if the officials are alert, if anyone gets gassed by CO when actually dealing with a fire or heating that is a mining risk which has to be taken, but even then it should not prove fatal as everyone knows that the risk is there and if small birds are kept on the job, as the law demands that they shall be, they will be the first to suffer and the men can be withdrawn before they are seriously affected

The danger from CO_2 is rather more insidious as this gas has no smell and lies in any old unventilated workings of a mine, it should of course be found by the supervising staff on their inspections, but cases arise where men go into old workings for some reason without thinking of the danger and are overcome.

Accidents due to fires, ignitions and explosions

The above subject has been dealt with in detail in my paper 'Fires and ignitions in mines' which is before this meeting, so I do not propose to deal with it any further except to remark that while accidents under these headings are the most arresting and startling they actually do not account for as many fatalities in a normal year as do falls of roof and side or haulage accidents.

Means of increasing the safety in mines

The two most important factors bearing on the safety problem are research and education, a tremendous amount of research has been done in England by the Safety in Mines Research Board, and in other countries by similar bodies, and the industry is benefiting greatly by their labours, explosives, method of dealing with coal dust, heatings, haulage safety appliances and safety clothing are all subjects on which valuable work has been done and extremely valuable information obtained.

Education is another extremely important factor in safety in mines and one that is rightly receiving increasing attention in this country, for example, shot-firers are now being trained up to pass an examination qualifying them for their position, there is no doubt that if one can get the officials and workmen to appreciate more vividly the dangers inherent in the work of coal mining the accident rate will decrease.

PACKING WITH INCOMBUSTIBLE MATERIAL IN COAL MINES.

By L J BARRACLOUGH,* M Sc, M I Min E.

1. *Historical.*

The winning of underground coal seams is conducted by two main systems of working (*a*) Bord and Pillar, and (*b*) Longwall

The Bord and Pillar system has other names such as Room and Pillar, Stoop and Room, Pillar and Stall, etc —all of which indicate the general idea of comparatively narrow drivages or galleries which block out the coal area into Pillars or Stoops which may be extracted subsequent to the driving of the galleries

In the early days of English mining the pillars were left standing with a view to preventing accidents from falls of ground, economising in timber supports, and preventing surface subsidence, and under present-day conditions in the U S A, India and South Africa these considerations still apply, with resultant loss of the valuable coal pillars

The Longwall system of working has now replaced the Bord and Pillar system in English and Continental mines, in this method of work the whole of the coal seam is worked by long faces, the strata above the seam being supported temporarily by props and permanently by packs The roadways serving these long faces are formed out in the packed areas as the face advances, the roof or floor in these roadways being 'ripped' or excavated to give the necessary height and width for the working of tubs or conveyors and the passage of the ventilating air current

The success of the Longwall system of working largely depends on the efficiency of the packing or stowing of the excavated areas As the coal is extracted the immediate strata converge, tending to close the excavation, if this convergence of the roof and floor becomes excessive accidents from falls of ground frequently occur, the coal is worked with difficulty, roadways cannot be maintained and there is a danger of large bodies of inflammable gas being emitted and fouling the ventilation currents Of such importance is 'Roof Control' or 'Strata Control' in Longwall mining that in 1929 the Safety in Mines Research Board appointed a highly qualified Chief Mining Engineer and a staff of coalfield engineers to study the problems of packing and strata control, the various reports issued by the Safety in Mines Research Board on the subject afford very valuable information to the mining engineer.

In India the subject of stowing has been prominent before the mining profession of recent years and the Coal Mining Committee in its report of 1937 dealt with many aspects of the problem

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* Messrs. Andrew Yule & Co., Ltd.

VOL. VI—No. 3. [Published August 22nd, 1940.

2 *Objects of Packing*

It is generally agreed that efficient stowing of areas from which coal has been worked gives the following advantages —

(1) The filling of the wastes or goaves prevents accumulations of inflammable gas and eliminates 'weights' and large collapses of roof which might expel large volumes of gas into the working areas with consequent increase in the risk of explosion

(2) Spontaneous heating of coal or carbonaceous matter in goaves (gob fires) is eliminated

(3) No pillars of coal need be left to support the surface and coal may be worked under the sea or riverbeds and under occupied areas or industrial works

(4) The ventilation of the workings is improved

(5) The maintenance of the strata in an unbroken condition reduces the risk of the miner being killed or injured by falls of ground

(6) With intensive support intensive methods of working can be adopted, the number of roadways and haulages can be reduced, increased efficiency and economy result and supervision can be more effective due to the reduction in the area of workings to be inspected

3 *Methods of Stowing.*

There are four main methods of packing (*a*) Hand Packing, (*b*) Hydraulic Stowing, (*c*) Pneumatic Stowing, and (*d*) Mechanical Packing

(*a*) *Hand Packing* may be done.—

(1) with imported materials alone;

(2) with materials obtained from rippings of dummy or main roads (brushings) or back rippings, with material obtained from controlled falls in the goaf, with materials rejected *in situ* whilst working the seam, with chocks or cogs;

(3) with a combination of materials obtained under (1) and (2).

System (1) is rarely practised in British or Continental mining as the seams are thin (generally below 6′ thick) and the roof or floor strata have to be ripped to make and maintain roadways of adequate dimensions. System (2) is the common practice, strip or partial packing being employed to give controlled convergence of roof and floor. In certain seams notably in S. Wales, material is imported to supplement materials obtained under system (2). In Germany, where the Mines Police at one time insisted on solid packing, there has been a notable change over to partial or strip packing.

Where the materials are weak, *i e.*, where good stones for building the pack walls cannot be obtained, the pack walls are sometimes built of bags filled with small debris or the packs may be reinforced by wire mesh, or by wooden cogs.

Cost of Hand Packing—With materials readily available close to the site of the pack being built, *i e*, within 6′ to 8′, a good workman (in England) can well pack 200 cu ft per 7-hour working shift At a wage of 8 shillings per day this constitutes a charge of over 1*s* per ton of coal won, if solid packing is done If materials have to be imported the cost is increased by approximately 50% With partial or strip packing, in which material is obtained from dummy road rippings or controlled goaf falls, the cost of packing varies according to the percentage area packed but generally in seams of moderate thickness with shale roofs is 9*d* per ton, in exceptional cases, *i e*, a thin seam 3′ thick with strong sandstone roof with 4-yard gob packs and 16-yard wide gobs, the cost was from 4*d* to 5*d* for packing, excluding packs built by main road rippers

The cost of solid packing by bags is excessive, a bag 32″ × 14″ wide, costing approximately 2*d*, gives when filled a builder 30″ long by 12″ wide by 6″ deep The cost of bags alone approximates to 4 shillings per ton In practice bags are used only as pack walls which confine hand-packed small debris and even then the cost of bags is high

Limitations of Hand Packing—In seams over 6′ high good hand packing is rarely practicable In thick seams the cost of stowing increases rapidly for each foot of height over 6′

Hand Packing in India—Materials for packing are rarely available underground as rippings are not taken and the seams are fairly clean The labour force underground is composed of men small in stature and in the main unaccustomed to shovelling A rough estimate of the cost of hand packing in India, in a seam 12′ to 16′ thick, of which 25% has been taken in first workings, is 12 to 16 annas per ton plus capital charges and the underground labour force in a mine turning 1,000 tons per day would have to be augmented by from 750 to 1,000 extra underground workers

In our present Indian mines the tramming grades would prove a great obstacle to taking materials for packing into working faces and it appears obvious that hand packing on a large scale in thick seams is impracticable in this country

In thin seams 6′ thick or under, partial packing and controlled convergence may be accomplished by dummy road rippings or controlled goaf falls at a cost of 6 to 8 annas per ton of coal in virgin workings Such seams are rarely worked, and the labour personnel is unsuited to such work as yet.

(*b*) *Pneumatic Stowage*—Pneumatic stowage is a system whereby stowing material is conveyed through pipes by compressed air and delivered with some force to the place being packed. The material has to be graded and the length of pipes, and curves in them, limited

In Great Britain the system was tried at a colliery near Manchester and was abandoned, and it is now in use at a colliery in Fifeshire

In Germany various pneumatic stowage machines of the Torkret, Miag Konig and Biem types are being used, whilst at a colliery in Rumania experiments are being conducted in blowing material from the surface *via* pipes to the underground workings

At a Ruhr Colliery visited by the writer a Biein machine was stowing 200 tons per day Dirt up to 3" mesh was taken in tubs in the upper level, tipped by a side tippler on to a short belt conveyor which delivered the material to the stowing machine. The material was fed through the machine into 6" pipes, maximum length 300 yards, air pressure 55 lbs per sq inch, on to the face With the special layout the number of men required per shift for stowing 200 tons maximum was 17 Compressed air consumption was heavy and cost of pipe renewals and bratticing likewise

At a Scottish Colliery working a thick seam a pneumatic stowage installation is working and the following notes apply to it.

Wet sand was not delivered satisfactorily but dry sand proved suitable except that it was not jammed tight against the roof, and a considerable quantity of sand was blown on to the working face by the compressed air jet

The maximum capacity was about 25 cu yds per hour and air consumption 2,500 cu ft per minute, some sparks were given off at the delivery end but it was stated these would not ignite gas It is to be noted, however, that Audebost and Delmus in France must have had some grave doubts as to the danger from sparks from pneumatic stowing apparatus when they suggested that pneumatic stowage should be prohibited and 2 explosions, one in Lancashire and one in France, are attributed to such sparks In gassy mines, therefore, the introduction of pneumatic stowage has to be viewed with suspicion.

Summary —Pneumatic stowage does not appear suitable for general Indian mining conditions owing to —

(*a*) High cost of compressed air
(*b*) High initial outlay
(*c*) Difficulties in adapting existing layouts for transport of material to site
(*d*) In gassy seams the possibility of gas ignition by sparks
(*e*) High cost per ton of material stowed.

In certain special cases it may be applicable, however

(*c*) *Mechanical Stowing* is still in an experimental stage but at the Rheinpreusen Colliery, Ruhr Coalfield, turning out 3,000 tons per day, it has replaced hydraulic, pneumatic, and hand stowage

In this system the material is delivered at the tail end of a face belt conveyor and is automatically dumped off the belt at any predetermined place on the face on to a high speed throwing belt which delivers the material to the goaf Wet material can be handled up to 3" cube in size The machine can be electrically driven and has delivered 70 tons per hour. At Rheinpreusen Colliery the cost of stowing 100% solid with this system, including power, depreciation on machine (25% per annum), replacement of stowing belt (every

40 days or 16,000 tons), all underground labour for delivery material and stores was given as 0·4 marks per ton of coal (approximately 5 annas).

It appears the mechanical throwing belt has a future in this country in virgin areas where an intensive mining system can be laid out to suit it but it is not entirely suitable for collieries already laid out

Hydraulic Stowage—The objections to, and difficulties attendant on, hydraulic stowage in British and Continental mines are well understood and except in Silesia and the Myslowitz mine it has tended to be replaced by hand, pneumatic and mechanical stowing

The main difficulties attending hydraulic stowage are:—

(1) The effects of water on weak floors and roofs, rapid floor heaving and deterioration of weak roofs rendered it unworkable in many cases

(2) Difficulties in supplying suitable stowing material Washed sand, which permits of ready drainage of clear water, is the ideal filler for this system

(3) In thin seams, *i e*, under 4′ thick, with weak roofs, there is difficulty in packing close to the face, only small quantities can be packed per operation and there may be admixture of stowing material with the coal being wrought

These difficulties are not of grave import in India The roofs and floors of the seams are strong and are little affected by water, in many cases there are ample supplies of clean river sand which can be delivered fairly cheaply at the pit head; and in thick seams it is possible to flush continuously up to 4,000 tons of sand in one place

The cost of hydraulically stowing sand underground consists principally of

(*a*) cost of supplying sand to the pit head,
(*b*) renewal of pipes,
(*c*) pumping stowage water from the workings to the surface,
(*d*) barricade material to hold the stowage in place,
(*e*) labour for attending to pipes, flusher, pumps, etc

As may be judged from a consideration of the above factors the cost of hydraulic stowing will vary at each pit where it is practised One of the most important items, however, is the cost of delivering sand to the pit head, and in those cases where sand or other material is not available on or near site the cost of transporting the stowing material may be heavy.

4. *Research Work on Packing.*

The programme of researches carried out by the Safety in Mines Research Board may briefly be classified as—

(*a*) The physical properties of coal measure strata.
(*b*) Laboratory experiments to determine the resistances developed by packs, cogs and bag supports.

(c) Underground investigations The effects of depth, nature of material, thickness of seam, quality and extent of packing, rate of face advance, depth of undercut, line of face, width of working, the working of sub-jacent or super-jacent seams, inclination of seams, etc Associated with researches on packing are the studies connected with the resistances developed by face supports, the causes of weights, strata movements ahead of and behind Longwall faces and the development of suitable convergence recorders and dynamometers to measure height reduction and the resistances developed by various types of supports

The results of some of the investigations on hand packing are summarised below —

(1) Packs built close to the face and rammed tight to the roof, with intermediate crosswalls and face walls, gave the best results

(2) Packs should be built before cutting of the face is commenced

(3) Even in very well-built packs built by hand the percentage of voids was from 35 to 40

(4) The quality of the packing is all-important and well-built packs, though of limited dimensions, provided more efficient roof control than continuous poorly built packing, *i e*, well-built strip packs are preferable to poor quality solid stowing

(5) The rate of convergence associated with well-built packs was less than ½″ per foot of face advance, whether the face advanced quickly or slowly. Roof conditions are better on a slowly advancing well-packed face than on a quickly advancing badly packed face but where the packing was of equal quality the quickly advancing faces gave better conditions than the slowly advancing faces.

(6) Packs built of hard slabby sandstones developed greater resistances in the early stages of compression than packs built of rounded stones or of softer materials

(7) Cogs built of round timber and well filled with stone developed up to 6 times the resistance of an unfilled similar cog for the same extent of compression. An unfilled cog of round timber is of little value as a roof support

(8) 'Weights', phenomena characterised by a large increase in the convergence/advance ratio and often accompanied by widespread collapses of roof and emissions of gas, were the results of poor quality packing, in certain cases where the quality of the packing was improved 'weights' were eliminated.

(9) 'Bumps' are often associated with a lateral movement of the roof or floor in advance of the face by which stress is relieved but the inward movement of roof and floor was small.

There is not sufficient space in a short article to describe all the results so far obtained but some of the main features established by researches on packing are given above

5. *Difficulties associated with Stowing.*

At British and Continental mines stowing has been practised for several decades and systems of working have been evolved to obtain the full benefits for the expenses incurred in stowing As an example a case may be cited of a seam 7′ thick being worked on the Longwall system by conveyors and coal cutters; a double unit Longwall face 240 yards long is advanced 5′ per day and 850 tons of coal are loaded in 6 hours at one loading point The mechanisation of the coal winning operations, the high output per man, the concentrated work resulting in few roadways to be maintained and efficient supervision and a high degree of safety, combined with a low cost per ton, are dependent entirely on the efficient system of stowing, or roof control which is adopted In this case, although the cost of stowing is a high proportion of the total cost per ton of coal won, the advantages gained more than outweigh the disadvantages

In Indian mines many of which are now fully developed for pillar extraction the mines were laid out and development proceeded before the necessity for stowing was obvious, and in these mines the full benefits of stowing, apart from conservation of coal and increased safety, cannot be realised In new mines it may be possible to plan the workings so that some of the expense of stowing may be recovered by reducing other costs

As seams in India are generally thick, it is not practicable to rip the roof or the floor to provide stowing materials, hence material for packing will have to be derived from the surface. Some collieries at which sand or other material can be excavated and transported cheaply to the pit head can obtain their material for stowing much more cheaply than other collieries, where the transport of the material may be so costly as to render the cost of stowing prohibitive, unless some assistance is rendered

The method of stowing adopted depends on the conditions associated with each mine; no hard and fast rule can be laid down as to the best system of stowing. For Indian conditions in general, however, the system of hydraulic stowage appears the most suitable but there may be conditions where hand, pneumatic or mechanical stowage might be more cheaply applied.

6. *Conclusion.*

Efficient packing, whether solid or partial, ensures the extraction of the maximum quantity of coal with the greatest degree of safety and accordingly is to be recommended. Many difficulties have to be overcome, and much pioneering work done, before the system can be applied generally to Indian conditions but recent legislation should greatly facilitate the extension of stowing systems.

SOME PHYSICAL CONDITIONS WHICH AFFECT SPONTANEOUS HEATING IN COAL MINES

By W KIRBY, *B Sc*, *M I Min E*, *Chief Inspector of Mines in India*

Spontaneous heating in coal mines is of great importance on account of the considerable losses of coal involved in the resulting fires and the dangers incurred in dealing with those fires

The causes of spontaneous heating may be considered under two headings —(*a*) Physical, and (*b*) Chemical With the limited space at my disposal I propose to discuss the most important physical conditions in mines which are conducive to initiating spontaneous heating and which will be of more interest to the mining engineer than the chemical aspect of the subject

The physical conditions which influence spontaneous heating in coal seams might be classified as follows —

(1) The thickness of the coal seams
(2) Nature of the coals, geological conditions and the crushing of pillars.
(3) The nature of adjoining strata
(4) Depth of the coal seams

1 *The thickness of the coal seams.*

The thicker the seams the more difficult it becomes to extract all the coal, and some small coal is generally lost in the goaves, due to 'weight' coming on the small pillars or 'stooks', necessitating the leaving of coal in the goaves This coal becomes crushed and is one of the primary causes of the spontaneous heating Again, the cleavage planes in thick seams are usually very pronounced and may lead to deterioration of the pillars in the 'first working' particularly where the galleries have been driven to the full height in thick seams There are sometimes soft bands in coal seams, *e g*, No 15 seam in the Jharia coalfield, which deteriorate and are likely to create conditions conducive to spontaneous heating, because of the gradual weakening of the pillars which may result in collapses and the production of small coal and other conditions likely to promote heating

2 *Nature of the coals, geological conditions and the crushing of pillars.*

The nature of the coals and the geological conditions play an important part in the stability of pillars

The friability of coals varies considerably throughout the Jharia coalfield. In the eastern portion of the field there is a soft band, 2′–4′ thick, in the middle of 15 seam, which crumbles up in the hand, and the cleavage of the coal is also very pronounced These conditions encourage deterioration of pillars In the south-east part of the Jharia coalfield there is a 4′-5′ section of very

VOL. VI—No. 3. [Published August 22nd, 1940.

friable coal, about 12 feet from the roof and in addition the seam is traversed with slickensides, and these factors have an important bearing on the liability of the coal to crush and form small coal In the year 1932, I read a paper before the National Association of Colliery Managers (Indian Branch) entitled 'The Causes of Spontaneous Combustion underground in mines in the Jharia Coalfield together with a consideration of some preventive measures', in which I referred to an explanatory note on a geological section and the geological conditions in this part of the coalfield by Dr Fox, and I cannot do better than quote this note in full and give the section (Figure 1)

Dr Fox states —

> 'The section is drawn to the scale of 4 inches to one mile, both vertically and horizontally, on the line, roughly of longitude 86° 26′, across sheet No 8 of the Geological Map of the Jharia Coalfield The northern part of this section was dealt with in a special excursion of the Mining and Geological Institute of India on the 10th February, 1930 The intention of that excursion was to show that the gneisses of Pathardih were not the relics of an ancient ridge on which the Coal Measure sediments were laid down And it was proved on the ground that the coal bearing strata on each side of this Pathardih horst had not been let down by simple faulting The evidence was clear that shearing had occurred along the line of the gneiss-coal measure boundary, as though the gneisses had been driven westwards into the sedimentary rocks, or that the coal bearing strata had been thrust against the gneisses from the west (See *Transactions, Mining and Geological Institute*—Volume XXV, pages 176–179, 1931, and the Map of the Bhulanbarari area given with it)
>
> 'With regard to the area south of the Pathardih horst the outcrops of the seams do not show the same spectacular sweep as they approach the gneisses In fact, at first sight there is apparently strict parallelism between the outcrops and the boundary, such as would be expected with beds gently dipping away from the rocks on which they rest undisturbed The first irregularity, however, becomes evident in tracing the outcrops of No X and No XI/XII seams from west of Sawardih to Chasnala They converge eastward, and so does the outcrop of No XIV seam with respect to that of No X seam There is little evidence of faulting between Examined closely it is found that faults must exist between each of the seams named—between X and XI-XII near Chasnala, and between XIV and XI/XII south of Sawardih When the thickness of the beds and the dips of the strata are carefully drawn in section it is discovered that there are irregularities between XV seam and XVIII seam in the Sudamdih tract. And the mapping has shown unusual seams and beds above XVIII seam in the area south-east of Sitanala
>
> 'The explanation of these features is difficult but the clues are to be seen in the banks of the Damodar river south of Tasra (23° 38′, 86° 28′) and also north-east of Bhojudih railway station In each case the strata are found striking almost at right angles to the direction of their outcrops at Sudamdih and Chasnala. The dips increase steadily from Pathardih to the south bank of the Damodar by the railway bridge, but at no place are the dips as steep as those seen south of Tasra. And just east of Bhojudih the dips are not only up to 80°, but the strike has swung round so as to give definition to a deep trough to the west under Bhojudih and onward. Crushed coal in a seam on the banks of the Ijri further confirms the synclinal structure west of Bhojudih. All these evidences are depicted in Sheet No 8 of the Geological Map of the Jharia Coalfield. And there can be no question that the evidence as a whole confirms a westward forcing in of the gneisses or an eastward thrust of the Gondwana strata.
>
> 'On pages 87-88 and 151-152 of the memoir on the geology of the Jharia coalfield (*Memoir, Geological Survey, India*, LVI, 1930), questions of shearing along the bedding

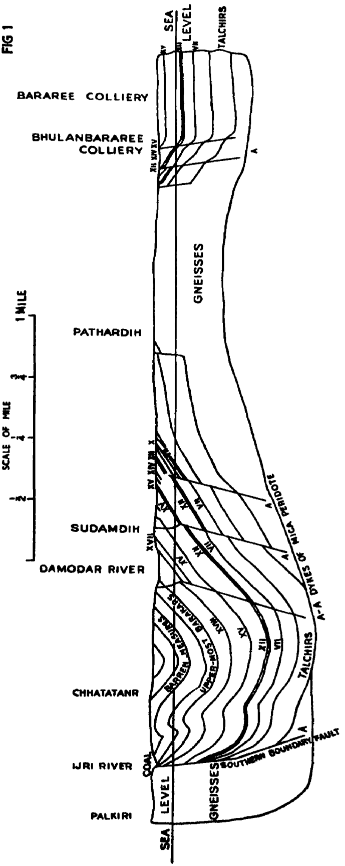

FIG 1

SECTION PALKIRI AND SUDAMDIH TO BHULANBARAREE of the strata are considered The question to be decided is along which of the beds—sandstones, shales or coal seams—is sliding likely to occur The general opinion from experience is that the plane between a thick sandstone and a bed of shale is most likely to function as a gliding or shear zone In this case the strata themselves will not be greatly affected if the folding or sliding is not excessive On the other hand there is little doubt that if a coal seam becomes involved in a shear zone the coal will be seriously affected by almost the smallest movements The result will be that any cohesion or strength of the coal will be greatly reduced and it is doubtful if any reliability can be placed on such material to withstand roof weight Of actual data in this connection we have evidence of two kinds—one in the curious failures of coal pillars in *certain* seams in *certain* areas, and the other in the liability of the same seams to ignition by spontaneous combustion

'In the last paragraph emphasis is intended on the word certain It is well known that the coal in the various seams in the Barakar series in the Jharia coalfield is not the same In some it is dull and hard and strong, in others it is bright and brittle and friable Taking these extremes as types of two seams it is evident that under stresses inducing a strain along the bedding of the seams the bright coal will shear rather readily It is nearly always the better quality coal Consequently, when such a seam is opened for working, the pillars will be subject to spalling, collapses are likely to occur in an inexplicable way to those who do not appreciate the loss of cohesion that has occurred in the geological past, and, lastly, such coals will readily oxidise and heat up and ultimately ignite with access of air It is true that nearly all bright coals with a volatile percentage over 25 are liable to spontaneous combustion, under suitable conditions, even when in undisturbed seams But when shearing, especially relatively slight shearing (enough to impair the strength of the coal), has taken place these seams are much more liable to fire when worked by the pillar and stall methods now in vogue in the Damodar valley coalfields

'The section which accompanies this note is to indicate the geological structure along one line from the southern boundary fault near Bhojudih northwards through Sudamdih and through the gneissic horst of Pathardih to the coal measures about Bhulanbarari It is by no means certain that over-riding is absent in the Barren Measure sandstone about Chhatatanr, and the considerable thickness of strata which has been designated Upper most Barakars may also be due to a duplication of the measures as the result of over-riding (as explained on page 88 of the Jharia memoir already referred to) With regard to the fault immediately north of Sudamdih there seems little doubt that over riding has occurred and that this is not a normal but an overthrust fault It must, however, be kept in mind that the direction of shearing (over-riding or overthrusting) is not merely up and down along the fault plane, but that the greatest movement appears to have been along a horizontal direction in the shear or fault plane This is very hard to detect in the field unless the face of the fault is seen, but the mapping of the surrounding areas leaves no room for doubt It is to be noted that the intrusions of peridotite have occurred after the strata were disturbed and dislocated by tectonic movements—probably while the Barakar coal seams were still overlaid by 10,000 feet or so of younger strata.

'With regard to the whole question of structure of the Jharia coalfield there is abundant evidence of shearing in several places, both in the south and east as well as to the west of the field. At the point of the Pathardih horst in the Bhaura (Bhowra) area the gneisses appear to have ploughed under the coal measures. And in each case which has been scrutinised the evidence points to a general compressive effect along an east-west direction, i e, roughly parallel to the main line of faulting It seems that the great boundary fault is the chief tectonic feature, and that along this line the strata on the down-throw side has not been let down equally all along In consequence of this there are deep sags—now the coalfields of Raniganj, Jharia, Bokaro and Karanpura—and in these sags over-riding has followed the bending of the strata—the successive (or certain) beds slipping (or shearing) over the next below—as already referred to on page 88 of the Jharia memoir.

All these subsidiary movements combined are not easy to unravel, but the sum effect has been communicated to certain coal seams in certain areas, and those coal seams in those areas are both liable to spontaneous combustion and to collapse to a greater degree than should normally be expected'

Shale and sandstone bands in seams are likely to affect the liability of a seam to heat spontaneously, as when coal is crushed and heat generated, the shale bands, which are poor conductors of heat, are likely to retain the heat and assist spontaneous combustion In the Jharia coalfield fourteen fires have occurred after premature collapses of pillars have taken place and there is no doubt that the friability of the coal and the geological disturbances were important contributory factors

Dr Penman, in Table II of his paper* 'The Crushing Strength of Coal Pillars', gave the approximate average crushing strength of pillars in lbs per square inch for Nos 15, 14 and 13 seams in the Jharia coalfield, as 1,000, 1,100 and 1,050 It is significant that these three seams which are the most liable to spontaneous combustion have the lowest crushing strengths of the coals given in the table

The crushing of pillars may be directly responsible for fires I know of one case in the Jharia coalfield where a pillar in 15 seam adjoining a depillaring area at a depth of 550 feet was badly crushed and eventually the pillar went on fire spontaneously The effect of crushing is to produce small coal and also to generate heat due to the grinding action produced

In Volume LXIV (1922-1923), *Transactions of the Institute of Mining Engineers*, Prof Briggs gives the results of experiments carried out on the heat generated by the crushing of coal, and he states, 'A fragment of average Bituminous coal 1/300th inch in diameter, if suddenly produced by crushing, will, in the midst of similarly conditioned particles, obtain a temperature rise of 52°F If the waste in which the crush takes place has a temperature of 75°F, this particle will thus be raised, practically instantaneously, to a temperature of 127°F. Under the same conditions a fragment 1/100th inch across will attain a temperature of about 92°F'

The heat generated accumulates in the small coal produced and as the temperature increases the affinity for oxygen increases, until the temperature of ignition is reached The most important factor in the crushing of pillars is the small coal produced which is so much more susceptible to oxidation than coarse coal

3 *The nature of adjoining strata*

Spontaneous combustion is greatly influenced by the capacities of various strata for conducting heat Ordinary shale, still air and coal are bad conductors of heat, while sandstone is a good conductor. Herschel and Lebour (*Transactions of the Institute of Mining Engineers*, Volume LXIV, 1922-1923, Briggs, Spontaneous Combustion, initiated by crushing) show that ordinary coal measure shale is not such a good conductor of heat as coal (unspecified) and that soft sandstone is twice and hard sandstone three times as good a conductor as coal

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* *Transactions of the Mining and Geological Institute of India*, Volume XXV.

These differing conductivities have an important influence on spontaneous heating Take for example the 3-ft shale roof, which is of a carbonaceous nature, above No 15 seam in the Bararee-Bhulanbarari area It is very probable that this shale has contributed greatly to the initiation of spontaneous heating in some instances There is also the 7-ft 'parting' between Nos 15 and 14-A seams. Then there are the shales, chiefly of a carbonaceous nature, between Nos 14 and 13 seams At Gopalichuck this 'parting' varies from 3′–14′ At Ekra it thins out to about 6′, combined with a 2-ft sandstone band At Mudidih it thickens up to 14 feet

I quote these examples to indicate that seams with adjoining beds of shale should be treated with suspicion For instance, if No 15 seam is being depillared and as much coal as possible has been extracted, there is the 3-ft. shale roof which is always a potential danger Accumulated masses of fallen shale roof may lie in the goaves for months, covering small coal, which readily oxidises The shale being a poor conductor of heat will not allow the heat produced by the oxidation to be dissipated, as it is generated, which results in the shale and coal reaching the temperature of ignition Analogous conditions exist where there are contiguous seams with 'partings', consisting chiefly of shales On the other hand if the adjoining strata are sandstones, there is not the same tendency for the heat to be retained, as the sandstones are comparatively good conductors of heat

At two mines where fires have occurred in the goaves of No 14 seam, the shales between Nos 14 and 13 seams have fired on the surface when thrown on the 'spoil heap', indicating that they are liable to self-heating due to their carbonaceous nature. I am of the opinion, therefore, that many of the shales in the Jharia coalfield have played a considerable part in the development of spontaneous heating due to their insulating properties and their composition.

4. *Depth of the coal seams.*

The greater the depth of the coal seams the greater is the liability to crush and form small coal due to the pressure of the superincumbent strata. Even where pillars of adequate size are left for the particular depth worked the coal may be of a friable nature and 'shedding' may take place, resulting in the gradual deterioration of the pillars. At great depths where there are extensive workings there may be difficulty in adequately ventilating the workings so that heat created by crushing or goafing operations may not be readily dissipated

A detailed study of the physical conditions prevailing in coal seams is essential when considering the causes of spontaneous combustion underground, and the means to be adopted to prevent these spontaneous heatings.

FIRES AND IGNITION IN MINES

By E B. PARK *

The heading of this paper covers a wide field, embracing as it does cases of spontaneous heating without actual fire, blazing fire, which may be due to spontaneous heating or to some mechanical or electrical cause, ignition of gas with subsequent flame but practically no explosion and ignition of gas or coal dust with a more or less severe explosion

Spontaneous heating —This is quite a common occurrence in coal mining operations although it is one of the things which the Mining Engineer takes the greatest precautions to prevent

Cause of heating —Coal in its natural state always absorbs oxygen and in doing so a certain amount of heat is generated, unfortunately coal is a very bad conductor of heat and the heat thus formed is not easily dissipated, with the result that the temperature rises and this is immediately followed by an increase of the rate of oxidation thus producing more heat until finally ignition temperature is reached

Liability to heating of different seams —Different seams of coal vary greatly in their liability to spontaneous heating and this is chiefly due to two causes (*a*) the thickness of the seam and (*b*) the physical constituents of the coal (*a*) It is a well-known fact that in thin seams 4′-0″ thick or less, spontaneous heating is very rare indeed, this is of course to be expected as the heat generated by the oxidation of the coal is dissipated through the roof and floor of the seam and also there is not the same quantity of coal lost in mining operations as there is in a thicker seam. (*b*) Coal consists of 4 physical constituents—Clarain, Durain, Vitrain, and Fusain—and of these four constituents it is the last, Fusain, which is primarily responsible for the spontaneous heating as it absorbs oxygen far more readily than any of the other three constituents In addition to its affinity for oxygen the Fusain in a coal seam also tends to create spontaneous heating because it is the softest part of the coal and coal with much Fusain in it is softer and therefore more liable to disintegrate than coal which has little of this constituent, *e g*, Anthracite which contains no Fusain is not liable to spontaneous combustion at all, this disintegration of the coal exposes more coal surface to the air and therefore the rate of oxidation of the coal increases.

One other factor which has a definite bearing on the liability of a coal seam to spontaneous heating is the nature of the floor and roof· if the floor and roof are composed of sandstone or some similar rock which is a good conductor of heat there is definitely less likelihood of spontaneous heating

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* Loyabad Colliery, Manbhum.

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than there is if they are composed of shaly material which is a bad conductor of heat

Rate of progress of spontaneous heating—The rate of progress of a spontaneous heating until it becomes a blazing fire varies considerably depending on several factors (*a*) the degree of spontaneous combustibility of the particular seam, (*b*) the amount of the coal concerned in the heating, (*c*) the state of disintegration of the coal, (*d*) the amount of oxygen that is available for the coal to absorb, *e g*, there is more likelihood of heating developing in a seam which requires a high watergauge to ventilate it than in one with a low watergauge, other things being equal

As spontaneous heating starts and developes in a mine it produces effects which enable an experienced mining man to detect it in most cases before it becomes a blazing fire, although in cases where oxidation is very rapid this is not always so.

The definite stages of a heating can be classified under the following headings

1st stage	Sweating, or deposition of moisture on the roof, sides, etc
2nd ,,	'Gob stink' smell produced
3rd ,,	Paraffin or petrol smell produced
4th ,,	Burnt tar smell produced
5th ,,	Smoke appears
6th ,,	Flame visible

'Gob stink' so called because heating usually occur in the goaf or 'Gob' has a very distinctive odour and an experienced man can detect the very faintest trace of it by his sense of smell and if even the faintest trace is detected it is absolutely infallible proof that a heating is starting It is safe to say that over ninety per cent of fires in mines that are caused by spontaneous heating are discovered by some one detecting a smell of gob-stink in the mine, the remaining small percentage are exceptional cases where the air getting to the heating is under pressure of some kind and development of the heating is so rapid that when it is discovered it has already reached one of the more advanced stages outlined above

Other fires in mines—Fires other than those caused by spontaneous combustion may be initiated in a variety of ways which it is convenient to classify as 'Mechanical' and 'Electrical'

Mechanical initiation of fires—In the majority of cases this class of fires is caused by some kind of mechanical friction which continues over a period of time until sufficient heat is generated to set alight any combustible material which may be near at hand The most common instances are the rubbing of a continuously running endless haulage rope on a defective pully which has ceased to revolve or on some obstruction such as a sleeper which has got out of position, the rubbing of a steel jigger face conveyor on timber due to the conveyor being improperly built up or having been pushed out of alignment by shot-firing or some other cause, to the rubbing of an endless belt conveyor on part of the steel framework which has got out of alignment or been damaged, or on some projecting piece of wood which is fouling the conveyor, again if a belt conveyor is badly overloaded the belt may be continually slipping on the driving drums and eventually generate so much heat that if there happens to be any very inflammable substance close to it this is set alight

Other causes of initiation of fire which come under this heading are defective or damaged safety lamps or of course in open-light mines the naked lights used by the miners Actually a defective safety lamp is not likely to cause a fire in a mine unless it is in a place where there is some gas, in which case it may ignite the gas and cause a fire or an explosion, but there have been cases when miners' clothes have been hung over a safety lamp with the result that the latter has become red-hot and set the clothes alight, though this is an extremely rare occurrence

Electrical initiation of fires —The initiation of fires by electricity without the presence of either gas or coal dust is uncommon because if there is a defect in the electrical apparatus and a flash occurs this is of such a short duration that it must be in contact with something that is very inflammable for a fire to be started; the usual medium of propagation of the flame is either oil or oily waste or rags which have been left lying about near to the electrical apparatus by some negligent attendant and it is most essential that where there is electrical apparatus in a mine the place in which this apparatus is housed shall be kept as clean as possible

An occasional source of serious trouble in this way is a transformer and in this case there is always oil in the transformer itself, this is set alight and causes an alarming fire, when transformers are in use underground they should be kept in a completely non-inflammable house and no inflammable material must be kept in the same house

Another occasional source of an electrical fire is a defective cable which bursts, this is always due either to serious overloading of the cable or to some mechanical damage which causes the insulation to break down, the flash that occurs will sometimes set fire to the paper insulation in the cable and thus initiate a fire especially if, as is quite a common practice in this country, the cable is supported on wooden pegs let into the coal sides of the roadway, these pegs often get very dry and readily propagate the flame once it has started and if they become properly alight and no one discovers the fact there is every likelihood of a serious fire occurring

Open-light mines —In mines where safety lamps are not used the ordinary lamps carried by the workmen are in themselves an obvious danger as they are liable to set alight any dry inflammable material with which they come in contact and it is really rather surprising that cases of initiation of fires are not more numerous than they actually are in these mines; the saving factor really is that in the majority of mines where no CH_4 is found, and therefore open lights can be used, there is more or less percolation of water throughout the mine and the damp atmosphere renders anything in the mine far less susceptible to ignition than it otherwise would be.

It is an old saying in the mining world that you do not usually get major trouble from 'gas' and 'water' in the same colliery but that you are very lucky if you have not trouble from either one or the other; it is this water in the non-gassy mines which is the great safeguard against fires being caused by the open lights

IGNITION OF GAS AND COAL DUST

Ignition of gas —Ignition of gas (CH_4) can occur in a mine either with or without a more or less violent explosion It is a well-known property of CH_4 that it is only explosive between the limits of a 4·5% and 13 5% mixture with air, and it is not uncommon for an accumulation of gas to be ignited in a mine without causing an explosion at all, this is I think usually the case when an ignition of gas occurs in an open-light mine as in these instances there is almost always just an isolated pocket of gas in a certain part of the working but nothing at all in the general body of the air, with the result that if some source of ignition such as an open light comes in contact with the gas the latter just bursts into flame and burns itself out without causing an explosion, the classical example of this kind of ignition was the custom that was prevalent in the old days when a miner before starting work deliberately used to light up the gas in his working place by holding his open light above his head while he himself crouched down and allowed the flame to pass over him, this removed any accumulation of gas and he could then carry on with his work without fear of further ignition as the movement of himself and his mates was sufficient to cause any gas which was given off to become mixed with the air and carried away

Now-a-days when the majority of mines are rather deep and liable to gas it is essential to have a system of mechanical ventilation by means of some kind of fan, in order to keep the working places clear, and it is unusual to find large isolated pockets of gas as it is diluted by the air as it is given off from the strata, but what usually occurs to cause an ignition is that through some cause the ventilating system fails for a certain part of the workings either through breakdown of the ventilator or more usually through the air being allowed to short circuit owing to some separation doors having been left open or broken, and in this case the whole body of air in a district, or at least a large part of it, becomes charged with the gas to such an extent that it is an explosive mixture, in these circumstances should any source of ignition be present a serious explosion of gas occurs

The most common causes of ignition of gas in a safety lamp mine are: (1) fires or spontaneous heating, (2) shot-firing, (3) electricity, (4) defective safety lamps

Ignition by fires or spontaneous heating—This is the most common and is liable to occur at any time when a heating or fire is being sealed off, there is always production of gas when coal is distilled by heat and as the area is sealed off the ventilation into the area is gradually reduced with the result that an explosive mixture may be formed and of course if this comes in contact with the heating or fire an explosion occurs

Ignition by shot-firing—Where shot-firing is done in a mine in which gas is found there is always a risk of an explosion because although the law insists on all possible safeguards being taken, such as only permitting the use of specially tested explosives, making the use of stone dust compulsory, prohibiting the firing of shots if any gas at all can be detected, encouraging the use of sheathed explosives and in various other ways, yet there is always the personal element present and a little slackness or fool-hardiness on the part of the shot-firer is liable to cause an explosion, for instance an improperly placed shot-hole or too large a charge in a hole will result in a blown-out shot producing flame and if the shot-firer has omitted to test for gas the result is an explosion, or again in firing in stone rippings in roadways behind a Longwall face if a break in the stone crosses the shot-hole and connects with the goaf the flame from the shot may ignite gas in the crack and cause an explosion of gas in the goaf

Ignition by electricity—As with shot-firing, so with electricity, it is always a potential source of danger in a gassy mine, because although the Electrical Engineers tell us that with really up-to-date protective devices and modern plant there should be no danger of an explosion, yet the fact remains that those protective devices again depend for their efficacy on the human element in setting them and keeping them in perfect adjustment and the human element is always liable to be at fault, especially in the dark conditions prevailing in a coal mine

Practically speaking any piece of electrical machinery, even when of the so-called 'flame-proof' type, may cause an explosion either because of negligence on the part of some electrician who has been examining or repairing it and who in putting it together again has not done so properly so that although it works quite satisfactorily it is no longer 'flame-proof', or because it has been damaged in some way by a fall of stone or coal or by a derailed set of tubs. Instances are on record when even cables which have been damaged or overloaded have burst and started a fire It is of course needless to say that if there is any gas present when a spark or flame occurs from the electrical machinery it ignites at once and either explodes or burns according to the percentage present in the atmosphere.

An extremely good example of the circumstances in which ignition by electricity may take place occurred a few years ago when an in-bye auxiliary fan was shut down for a short time for repairs, after the repairs had been effected the switch was put in to re-start the fan, this sparked and an explosion occurred killing the men who were there. The stopping of the auxiliary fan had caused the ventilation in that particular part of the pit to be reduced with the result that the normal emission of CH_4 from the district was not sufficiently diluted by air and an explosive mixture was formed

Ignition of coal dust —It is of course a well-known fact now-a-days that dry coal dust, if in a sufficiently fine state of sub-division, is extremely explosive and in all countries where the coal mines are dry and dusty extensive precautions are taken to minimise the danger of explosions from this source by spraying water or spreading inert stone dust around the galleries of the mine where the coal dust collects, an explosion of coal dust is almost always far more violent and destructive than an explosion of gas alone and in fact practically all the really major explosions in coal mines have been coal dust explosions

In order to have a coal dust explosion it is necessary for the coal dust first to be raised up in a cloud and well mixed with the air and then, while in this state, for some source of ignition to be applied to it The most usual cause of an ignition of coal dust is by a previous ignition and explosion of gas as this provides the necessary violence to raise the dust in suspension in the air, and also the flame to ignite it, it is a fact that the great majority of coal dust explosions are caused by a previous small gas explosion

It is possible however for coal dust to be ignited without a gas explosion, *e g*, a blown-out shot may do it or some unusual occurrence such as happened not so very long ago when a set of loaded tubs broke away and after gathering speed piled up at a bend in the roadway where there was an electric cable, the coal in the tubs was tipped out by the crash and of course the fine dust rose in a cloud, at the same time the cable was broken and it emitted a flash which started an explosion This is an extremely unusual combination of events but things like this do happen and are of course extremely difficult to guard against

STORAGE OF COAL

By E R Gee, *M A. (Cantab), F G S , Geological Survey of India*

The main interest in the question of storage of coal lies in the fact that coals, particularly those of low rank—bituminous, sub-bituminous and lignitic—are liable to spontaneous combustion and also to deterioration both in their calorific values and coking propensities This is due to the fact that coals, especially the types mentioned above, absorb oxygen slowly and in the process, as a result of chemical reactions, heat is generated

Formerly it was supposed that this generation of heat was due to the oxidation of iron pyrites in the coal and mineral matter and that the latter reaction was responsible for spontaneous combustion Although the possibility of the effect of this reaction cannot be overlooked in those cases where pyrites occurs in a relatively large proportion and in a finely divided state, yet it can scarcely explain the liability to spontaneous ignition in the case of many coals that are known to be low in that mineral, including many of the Gondwana coals of India The alternative explanation appears definitely more reasonable and is doubtless the main factor involved

In the case of Indian coals, the tendency to spontaneous ignition is apparently relatively greater in the case of the Raniganj, high moisture coals, than with the Barakar, low moisture seams

Although we are not yet in a position to speak with any degree of certainty on the question of the particular chemical reactions that take place gradually in the coal substance during the maturing of a coal seam, yet it appears that, while being transformed from lignites into sub-bituminous and bituminous types, certain complex chemical substances, which are particularly reactive to oxygen, are formed Further chemical change, into high rank bituminous coals with strongly caking propensities, apparently results in the conversion of these reactive elements into more stable substances and the change towards anthracitisation renders the coal still further immune to oxidation

Thus we find that the low moisture, well-matured bituminous coals of the Barakar measures of the Jharia, Giridih and Raniganj fields are much less liable to spontaneous combustion than the higher moisture, less matured, bituminous and sub-bituminous seams of the Barakar measures of other fields and of the Raniganj coal measures

Relatively high moisture appears to be related to the question of spontaneous ignition only indirectly owing to the circumstance that the state of maturity attained by these sub-bituminous and low rank bituminous coals corresponds with an appreciable moisture content.

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In connection with the question of spontaneous ignition in ships' cargoes, the data collected by two Commissions in Wales indicate that, apart from the chemical nature of the coal itself, fires may be expected to increase.—

(i) *pari passu* with the tonnage of the cargo and the temperature at which it is loaded,

(ii) with the fineness of division of the coal, and

(iii) with only *slight* ventilation during the voyage.

Also, the Commissions failed to find a single undoubted case of a spontaneous fire in a coal cargo having originated in any other place than under the hatchways, from which it follows that a heap of dust under the hatchways should be avoided

The question of the liability to spontaneous combustion in Indian coals and of storage, particularly when in a finely ground state, is important in relation to washing and to their use as pulverised fuel Regarding pulverised fuel, it would obviously be dangerous to store large quantities of the high volatile Raniganj coals for prolonged periods, and the direct firing system in which the pulverising mill and the burner is a self-contained unit may be preferable in many instances to the central grinding system which entails storage.

INDIAN EXPORT TRADE IN COAL

By C A. INNES *

It may be advisable to clear up at the outset of this article any possible confusion of thought regarding the coal shipment business, which is fairly substantial, and the coal export trade proper, which up till recently has been small In a country so large and also having so long a sea-board as India, and in view of the fact that the major coalfields are within a short distance of a large port, Calcutta, it becomes economical to route coal by sea and not by rail for the requirements of ports, and, in many cases, of the hinterland behind those ports The reason for this is that carriage by sea is cheaper than carriage by land The coal therefore for many of India's industrial concerns is supplied by ship from Calcutta, and among these may be mentioned the cotton mills of Bombay, the various railways in Kathiawar States, cement factories on the West Coast of India, and steamers' bunkers and harbour board requirements in nearly all India's ports

This business is generally referred to as the coastwise trade, and may be said normally to total, between Indian ports and excluding Burma, a million tons per annum

Shipments to Burmese ports were included in it prior to the year 1936, the year in which Burma was separated from India, but such shipments should now be classed as true exports, and are so classed in the statistics issued by Government In order however that the comparative figures given later may present a true picture, Burma has been regarded for the purposes of this article as a separate entity, and considered briefly 'in vacuo'.

Burma's annual consumption of coal is approximately 5½ lakhs tons, of which practically all is supplied from India, though metallurgical coke for the Burma Corporation is bought from the U K and from Africa as well as from India. The biggest buyers of coal are the Burma Railways, and the Irrawaddy Flotilla Co who operate a large fleet of river steamers on the waterways which constitute the country's highways. There is also a big bunkering business in Rangoon, mostly confined to the steamers of the B I. and Scindia. Competition from coals from Africa and other countries is but little felt, but wood and paddy husk are serious rivals to coal, and it is disappointing that the total exports from India of coal for the whole of Burma are not much more than half a million tons annually.

Turning now to the markets which have always been regarded as export markets, we may classify them under four heads; Ceylon, The Straits, which includes Singapore, Penang, Port Swettenham, Sabang Bay and rarely, Bangkok, the Far East comprising Manila and the Chinese ports; and Aden and ports west of India. These markets in the year 1920 took about 1½ million

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tons of Indian coal, but only just over a quarter of million tons the following year, and a mere 77,000 tons the year after So remarkable a change in such a short time could hardly come about through natural causes, and the cause actually was artificial, an embargo which the Government of India placed at that time upon the export of coal This embargo was considered to be necessary in the interest of Indian industries, as there was a serious shortage of railway wagons and available wagons had to be utilised for the internal trade, but there can be no doubt that it proved singularly unfortunate for the coal industry, which was thus suddenly deprived of a valuable market

When an import business which has been satisfactorily established is suddenly destroyed by the cessation of supplies, the importer is likely to turn elsewhere for the new connections which he has to make, and the door of markets previously held by India was thus opened to the coal exporters of South Africa and Japan It so happened that South Africa was at that precise moment considering how her coal trade might be expanded, and she was quick to seize her opportunity Substantial concessions in rail freight from colliery to port were granted to coal for export, and she soon succeeded in building up a large coal export trade, which at times has even encroached upon Indian coal in the ports of Western India Japanese coal, aided by certain favourable steamer freight conditions, had already penetrated as far westwards as Singapore, and was able to enlarge its interests on the withdrawal of Indian coal

The Government of India then made an effort to retrieve the position They appointed, in September 1924, the Indian Coal Committee to enquire what measures could be taken by Government, by the coal trade, by the railways, and by the ports, to stimulate the export of suitable coal from Calcutta to Indian and foreign ports The institution of the Coal Grading Board and concessions in railfreight and port charges on coal for shipment resulted from the recommendations of this Committee, and have been of much benefit to the coal industry, but this benefit has proved in practice to be principally in the direction of helping the industry to withstand competition from foreign coals at Indian and Burmese ports, and the assistance given was not sufficient to enable the export trade to recapture its lost markets

The cost of transport bulks largely in the price of coal c i f. destination port, and the comparative figures of distances from colliery to exporting port, and from exporting port to destination port, show that geographically speaking both Colombo and Singapore should be India's markets The difficulty of re-entering them has lain in the difficulty of dispossessing established connections, and, to a lesser extent probably, in the fact that the reputation of Indian coal for quality has suffered as the result of poor grade shipments made prior to the creation of the Coal Grading Board The Indian coal industry has however always hoped and felt that one day India would get back her markets, and that this extra million tons of business would help to rectify the state of overproduction in the industry.

In 1936 further assistance was forthcoming. Strong representations from the Indian Mining Association to the Railway Board and the Calcutta Port Commissioners were rewarded by the grant of a special rebate in rail-freight and port terminal charges of eight annas per ton on coal for export Immediately the Ceylon Government Railway contract was secured by India against competition from South Africa, holder of the contract, and this important contract, 1½ lakhs tons annually, has remained with India ever since Exports, which were only a little over 2 lakhs tons in 1935 and approximately the same in 1936, jumped to nearly 4¾ lakhs tons in 1937 and nearly 7¾ lakhs tons in 1938 for the first six months of 1939 they have been nearly five lakhs tons The assistance given came at the right moment as Africa towards the end of 1936 found herself so short of coal as to necessitate the restriction of exports, thus affording to India an opportunity similar to that afforded to Africa in 1922

The considerable increase in exports in 1938 is attributable to the Sino-Japanese conflict, which has put the Chinese coal industry out of gear Competition in this China business is keen, as Japan, America and Africa as well as India are out for a share of it, and the business is therefore not very remunerative, but it constitutes a valuable offtake which has played an important part in supporting the price of good quality coal for other business How long this business will continue is however problematical, it requires waters that are stormy, but not too stormy; it is likely to cease soon after the coming of peace to China, and is also likely to be curtailed by the slump in the Chinese dollar or by a Japanese blockade. With its cessation, any hope of maintaining the annual exports of Indian coal near the million tons mark also ceases

It does appear however that even then an average export of between four and five lakhs tons may reasonably be expected During the three years since the grant of the eight-anna rebate India has been able to consolidate her position in Ceylon, and to improve it in the Straits, Sabang and probably Manila, and the qualities of Dishergarh Seam Coal as a gas coal have received wider recognition than was previously the case Exports in 1937 approached the five lakhs tons mark, with practically no business forthcoming from China, and it seems therefore likely that this figure can be maintained after the China business ceases. In this connection it is interesting to note that the Committee of the Indian Mining Association, when addressing the Railway Board in 1936 to ask for the special export rebate of eight annas, stated that they hoped this would result in an extra three lakhs tons of export business, from which it appears that they then visualised a potential export trade of about half a million tons annually.

The figures of shipments to the respective export markets since 1936 may be found interesting; they are as follows:—

	1936	1937	1938	Jan.–June 1939
Ceylon .. .	1,62,040	3,69,280	2,72,514	1,62,230
Straits .. .	33,383	66,777	30,747	61,200
Far East . .	12,631	7,528	4,61,690	2,64,201
Aden and other Ports .	3,317	26,766	3,362	20

No account of the export trade would be complete without a reference to the work done for it by the Coal Grading Board The Board may be said to have regularised the shipment business, and the following tribute was paid to it in 1937 by the Committee of the Indian Mining Association in their memorandum on the Report of the Coal Mining Committee —

'The primary function of the Grading Board is to further the Indian coal export trade and protect the interests, in respect of shipment coal, of such buyers as are otherwise unrepresented in India by seeing that the quality of coal shipped is that which the buyer has bought and that the standard of loadings is maintained at the correct level. The work of the Board has resulted in the standard both of picking and screening for shipment coal being given most careful attention at collieries, which is undoubtedly a sound, if unobtrusive, form of advertisement for Indian coal Further, the Grading Board classifications are now known in export markets where Indian coal is sold, and furnish a satisfactory basis for transactions We consider therefore that the work which the Board has done and is still doing for the coal shipment trade is of great value———.'

In conclusion, various benefits which interests other than the coal industry derive from the export trade in coal may be mentioned. It contributes towards India's favourable trade balance It brings additional traffic to the Railways and the Telegraphs. It brings ships into Calcutta to lift the coal, which is a bulk commodity, and these ships, as well as bringing revenue to the Port and business to Banks, brokers, stevedores, ship-chandlers and others, pay income tax on their profits. It increases employment In short, it means to the country the advantages attendant upon a bigger export trade.

THE MARKETING OF COAL IN INDIA

By C. A Innes.*

Before coal can be put on the market, it has to be prepared for it, as different sizes are required for different purposes, whereas the coal as it comes up from the pit is usually a mixture of lumps and smalls, and also sometimes contains stone from the roof or from bands within the coal Well-equipped collieries therefore have mechanical screening and picking plants, on to which the coal is dumped from the tubs as they come up from underground, is sized by being passed through perforated screens, and is cleaned by the picking out of impurities by hand as it passes along the picking belt. It is then usually loaded into railway wagons direct from the plant

The sizes recognised in India have been defined by the Indian Mining Association, in 1932, as follows.—

	Class.	*Coal*
1	Steam Coal	Coal of a size larger than will pass through a 1" diameter round hole.
2	Export Steam Coal	Coal of a size larger than will pass through a 2" diameter round hole.
3	Slack	The undersized product separated from steam coal
4	Rubble	2"–¾"
5.	Small Rubble or Nut Coal . .	1½"–½"
6	Smithy Coal or Beans	¾"–⅜"
7	Small Smithy or Peas	½"–¼"
8	Dust	⅜"–0". Coal passed through a ⅜" screen.
9	Run of Mine or Sapta	The coal mixtures as mined.

In actual practice, however, few collieries can handle large orders for classes 5, 6 and 7, and contracts for rubble coal usually call for coal of size ¾" to 1½".

These different sizes serve different purposes in combustion, and though no hard-and-fast rule regarding suitability can be laid down, a very wide classification might be:

Steam Coal .. .	Loco, Bunkers, Domestic and some types of stationary boilers.
Slack Coal	Boilers with chain grate stokers, coke making cement kilns and brick burning.
Rubble Coal	Certain types of mechanical stokers, gas producers and forges.
Dust Coal	Brick burning.
Run of Mine	Stationary hand-fired boilers generally.

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VOL. VI—No. 3. [Published August 22nd, 1940.

So far as cleaning coal is concerned, picking is about all that is done in that direction in India, though in other countries washing is commonly practised in order to remove dross Coal companies in India have hitherto had little encouragement from consumers to instal expensive plants to improve the quality of their coal, as price is generally held to be of paramount importance in purchasing and the resultant very low average pitsmouth price of the past fifteen years or so in India—probably the lowest in the world—has not permitted the introduction of novel refinements This is a pity, as the long haulages and consequent heavy freight charges prevalent in India should encourage coal cleaning in order to minimise the amount of freight paid on dross, but the fact is that any industry, such as the coal industry in India, whose normal state is one of chronic depression, is disinclined to launch out into heavy expenditure which must increase costs when there is no certainty that buyers will be prompt to recognise and pay for the benefit they derive from it

The principal consumers in India are, according to 'Indian Coal Statistics, 1937'

The Railways with 32 9% of the total consumption
The Iron, Steel and Engineering Industries with 24 8%
Cotton Mills with 7 1%
No other industry exceeds 4% of the total

The biggest consumers, the Railways, are also the biggest producers of coal in the country, having large and well-developed collieries of their own. This dual rôle is largely responsible, in the opinion of the coal industry, for the poor price realised by coal in India, since the Railways as consumers naturally prefer prices to be low, and as producers can influence this to some extent by altering their ratio of coal purchased to coal produced, thus disturbing any equilibrium which there may be between demand and supply The Iron and Steel Companies also have their own collieries but both their coal purchases and their coal production are on a lesser scale than those of the Railways and cannot therefore exercise quite the same effect on the market

The system of distribution in India as between producer, middleman and consumer conforms to no rules Collieries which are grouped together under the aegis of a firm of Managing Agents have the advantage of a selling organisation which covers a wide field, both inland and abroad Such groups quote direct against most of the important tenders and to many of the big consumers, operate through agents and middlemen who may or may not be monopoly holders in certain areas, and also do business through brokers.

The function of the agent who, working on a commission basis, exploits a territory and often holds stocks on consignment for his principals is an essential one, but there is less to be said for the employment of middlemen who buy and re-sell. Their chief value is that they take the financial risk of giving credit to small consumers, their disadvantage is that they create extra competition at the expense of the producer Further, many of these middlemen actually own collieries themselves, thus creating a situation which seems somewhat anomalous, in view of the virtual impossibility of avoiding a divergence of interests on occasions

The small individual collieries which cannot afford an adequate selling organisation are dependent partly on brokers and partly on what share they get of the Railways' contracts, the coal industry's annual Lucky Dip Tenders for the requirements of the Railways from the market, usually about 3½ million tons, are called for in a lump in November or December A Railway order may mean to a small colliery the difference between working or closing for the coming year, and as there is no second chance once tenders are decided, competition is naturally keen, and this system of purchase is well adapted to take the maximum advantage of any weakness which there may be in the market

The policy of the Railway Board appears to have been for some years past to buy cheap inferior quality coal for the requirements of the State Railways, this policy is helpful to the small colliery inasmuch as most of the good quality coal is mined by the big colliery groups under Managing Agents and the poorer quality coal by the smaller independent collieries, and it has been followed so consistently that there is now an unusually marked cleavage in price between the two types of coals, since there no longer seems to be any point in cutting the price of good quality coals in the Railways' tender to try for business which almost certainly will not be forthcoming It is too early to say yet whether this means that producers of good quality coal are on the verge of freeing themselves from the bugbear of the Railways' tender, but the outlook appears hopeful, and this would certainly be conducive to the stabilisation of prices in the coal industry. It is time that the policy of forcing raisings to lessen costs in order to keep pace with falling selling prices gave way to a policy of maintaining selling prices by a controlled production, and that producers of good quality coal learn to put price first and volume of business second

SOME PROBLEMS OF INDIAN COAL.

By Amrit Lal Ojha, *M I.M E , F R.S A (Lond.).*

Little public attention has so far been focussed on India's importance as a producer of coal, for which her position among the coal-producing countries is apt to be underrated There is besides a paucity of literature on Indian coal Though India's average production stands between twenty to twenty-five million tons out of the world's total average of twelve hundred to fourteen hundred million tons, it is interesting to note that as a coal-producing country India stands second only to Great Britain in the British Empire and ranks ninth in the whole world. Besides being the chief fuel for numerous industries and domestic purposes the potentiality of coal as an important raw material for chemical industries has been in increasing evidence in recent times The National Institute of Sciences is to be congratulated on the timely endeavour to present to the public a comprehensive literature on coal dealing with its various technical and commercial aspects On the kind request from the Convenor, Dr C S Fox, I have decided to discuss in the following pages, only a few problems relating to Indian coal, leaving other topics on its trade and technique for more competent authorities to deal with The points I proceed to take up are (*a*) Railways and coal, (*b*) competitive conditions in the coal trade, (*c*) marketing of coal, and (*d*) the problem of conservation

(*a*) *Railways and Coal*

The historic relation between Railways and Indian coal is significant from many points of view It was the extension of the Railways to Raniganj that led to the rapid development of the coal industry The beginning of the coal industry dates back to 1774 But its growing importance began from the year 1885 when the East Indian Railway first opened its line up to Raniganj Before the advent of Railways there were serious transport difficulties and so the development of the coal industry was rather slow

Besides being responsible for developing the industry the Railways in India have, for some years past, been the principal determinant of the nature and extent of the trade in coal The ownership and management of collieries by the Railways themselves forms a long-standing controversy. In 1871, the East Indian Railway acquired large tracts of coal-bearing lands at Giridih for the purpose of raising coal for its own use At present, all the important Railways have got their own collieries. It is no doubt true that as a public utility concern Railways must be assured of continuity of supply of coal at a fairly steady price. It is also argued that the Railways are commercial enterprises and they must be free to develop their business interests and

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devise combinations of a vertical nature if they deem it profitable But the principle of the State entering into direct competition with private enterprise, purely from a commercial motive, has little justification from a social or economic standpoint except in a socialist regime I think there is much to be said in favour of a scheme of wholesale nationalisation of our mining properties (as has been recommended by the minority of the Coal Mining Committee) against the present arrangement of piecemeal socialisation which acts as a standing menace to the industry It is now high time to re-open the question whether the Railway collieries should be closed down The Coal Mining Committee also were not in favour of the proposal The best way in which Government can help the industry is to close down the Railway collieries for a few years, particularly in periods when the coal industry is in a bad way, or to work only one or two collieries and stop the rest, so that the outlook of the coal trade may be improved

Railway tenders and the working of the freight system have no less influence on the coal trade Railways are the principal consumers of Indian coal In 1935 they consumed 7,293,000 tons of coal or 31 9 per cent of the total, while in the same year they produced 2,725,000 tons of coal The internal price of coal is determined chiefly by the rates obtained at Railway tenders and industrial concerns refuse to contract at rates higher than the rates of the Railway Board The Railway Board cannot be credited with exercising this dictatorial power with an eye to the well-being of the industry Taking advantage of the weak organisation of the warring coal interests the Railway Board's policy has but tended to depress the price, especially in bad years A helpful re-orientation of the Railway Board's tender policy is a much-needed reform The present arrangement of State Railways buying two-thirds of their coal requirements from the open market should be increased by another million tons in order to extend appreciable relief to the coal industry

(b) *Competitive Conditions in the Coal Trade*

Competition, which is a common economic theory, makes for efficiency and hence a better trade outlook Unfortunately in the case of the coal trade competition has been the potent factor in hopelessly depressing the industry in every way Indian coal has to face competition both external and internal.

(i) *External competition.*

External competition virtually stopped our export trade in coal. The foreign markets have for long been the weakest spot of the Indian coal trade. It is here that the trade has suffered the worst vicissitudes It is true there is a small surplus of production over consumption in the country. But disposal of this surplus at remunerative prices is of vital importance to the whole industry. During the post-war period the Government of India placed a ban on the export of coal and the consequence of which was that South Africa captured our eastern export markets and even to-day we have not been able to regain those markets Loss of the export trade affected Bengal coal most seriously Due to the comparatively high Railway freights on internal movement of coal and the increasing tendency of industrial concerns in the heart and further ends of the country to have their coal supplied from collieries near at hand, Bengal and Bihar coals have to fall back upon the export trade As for quality and price, Bengal and Bihar coals enjoy definite advantage for export trade

The most disquieting feature of external competition is, however, the advent of South African coal in the western parts of the country, especially in Bombay and Karachi Bombay and Karachi consume 97 per cent of the total quantity of the imported coal High transportation cost makes it unremunerative for Western Indian concerns to replace South African coal by Raniganj or Jharia coal Freight per ton from Raniganj to Calcutta is Rs 3-12-0 whereas it is Rs 12-6-0 and Rs 15 for Bombay and Karachi respectively The secret of the competitive strength of South African coal is that it is bounty-fed Bounties are given in the shape of Railway freights which have little relation to economic rates There are three different coal rates, one for internal movement, another for coal intended to be bunkered and a third, which is the lowest, for export of coal to countries like India, Ceylon, Sumatra, etc There is another important circumstance which it is difficult to provide against, viz coal from South Africa is carried practically as ballast

(ii) *Internal competition*

In the internal market also the coal trade presents a spectacle of lack of organisation and cut-throat competition which entails in its train considerable loss of life and property Reference has already been made to competition from State-owned Collieries Apart from this, the competition for custom that exists among collieries owned by Limited Companies and Private Owners beggars description Under-quoting, rate-cutting and instances of similar unfair devices can be multiplied Responsibility for these evils must be attributed to the unorganised character of the industry and the absence of a central controlling authority The three Associations that exist can have no concerted plan of action Opinion is irreconcilably divided even among members of the same organisation Observing this confusing phenomenon of competition, the coal Mining Committee very aptly remarked 'The psychology of the trade is still too individualistic for concerted action even in its own interests'. The coal interests themselves are no doubt mainly responsible for this state of things. But an impartial critic would not let off the Government clean-handed I am not indulging in the too common practice of criticising the Government. But it must be admitted that Government have so far failed to protect the vital interests of the country connected with the coal industry. Governments in Great Britain, Germany, France and Japan were fully alive to the question and exerted their authority with legal measures, effecting regulation of output, allocating quotas, fixing minimum prices, control of tonnage, establishing Coal Mines Board with official patronage, enforcing compulsory co-operation among Private producers under State control, subsidising cartel formation and eliminating unhealthy competition It is indeed a sad commentary on our Government that they were too cold to feel the urgency for any such initiative and that they were instrumental in encouraging competition and scramble The three bodies interested in the coal trade of Bengal and Bihar jointly submitted a restriction scheme to the Government of India in 1933, which, for reasons best known to them, the Government did not consider it wise to accept and implement

The jute and tea industries here are perfectly organised Sugar and cement have excellent marketing arrangements The coal interests can profitably emulate their ideas In collaboration with the recently formed Stowing Board the three Associations should bring into existence a strong central organisation in the form of a cartel with necessary powers for regulating output, fixing quotas and minimum prices, etc, with a Marketing Board attached to it The evils of competition will be further minimised if tenders for Railways and other Government or semi-Government concerns are not entertained except from bona fide members of the Associations who are consenting parties to a working agreement of the nature indicated here.

(c) *Marketing of Indian Coal*

The figures of production and internal consumption of Indian coal almost balance each other This may lead one, unacquainted with the actual conditions prevailing in the coal market, to form a very happy picture of the Indian coal trade. The general conception that the demand for coal is inelastic is apt to lend an added support to conclusions of this nature. The fact is that there are certain extraneous factors seriously interfering with the market for Indian coal and this is why it cannot be disposed of so easily and profitably

A little over twenty million tons is India's average production The years 1937 and 1938 were exceptional, as the production of these two years exceeded twenty-two million tons. The annual consumption varies from a little over nineteen million tons to twenty-two-and-a-half million tons The annual export averages nearly 2 lakhs of tons. The annual import is to the extent of seventy to eighty thousand tons—the principal sources of import being in the order, South Africa (thirty to thirty-five thousand tons), United Kingdom (ten to twenty thousand tons) and Australia

(i) *Export Market for Indian Coal.*

The export trade in Indian coal assumed importance only in the five years ending 1900 when the average annual export figure was 30,500 tons. The peak in the pre-war period was in the year 1906 when over a million tons were exported For the decade ending 1915 the annual export average was approximately three quarters of a million tons 74,000 tons were exported in 1918, and 1920 saw exports mounting up to as high as 1·2 million tons Then came the official embargo which was not entirely removed till 1923 With the help of the Coal Grading Board, which was appointed following the recommendations of the Indian Coal Committee, Indian coal in recent years has no doubt made some headway in the lost markets

A minority of the Coal Mining Committee were definitely against stimulating the export trade in Indian coal In their opinion a stimulus to export was not only not worth giving but it was positively detrimental to the country's interest That the opinion, from a conservation point of view, is valuable cannot be denied. But in the present state of glut in the market with severe foreign competition we cannot do away with the export trade When the circumstances arise for a maximum utilisation of the entire coal resources of the country with the payment of adequate prices for all grades, then and then only should the question of stopping export trade be considered Export may be stopped at any time by the simple device of cancelling the rebates.

(ii) *The Story of the Internal Market*

Nearly 98 per cent of the coal produced in India is consumed within the country The largest consumers are the Railways with about 33 per cent of the total production The next in importance are the iron, cotton, jute and sugar industries which consume 40 per cent altogether Inland steamers, Tea Gardens and Paper Mills consume 4 to 5% Other forms of industries and domestic consumption account for 9 to 10% Consumption at collieries and wastage are estimated at 10%.

The problem of the domestic market is mainly one of finding a steady and economic price backed by unhindered movement of coal throughout the length and breadth of the country—free from such artificial restrictions as heavy freight and surcharge which reduce its competitive power to a considerable extent That the price of Indian coal during the preceding years was exceptionally low and sometimes uneconomic no one can deny Even the Coal Mining Committee, who could be little suspected of any sympathy for the Colliery owners, remarked 'there seems little or no margin of profit in the prices which most coal of good quality has been fetching during the past few years' For 1937 the average value of coal per ton in India was Rs.3-2-0, whereas in Great Britain it was Rs 10-2-0 and in Canada and South Africa Rs.9-5-0 and Rs 3-11-0 respectively.

The Railway surcharge though reduced at present to 12½%, together with the Existing Cess, River dues, etc, is a definite handicap and specially shuts out Raniganj and Jharia coal from western Indian markets. The coal interests were insistent on their demand for reduction of these transport charges Recently the Chief Commissioner of Railways is reported to have said that reduction in the coal freights had not been followed by any increase in traffic and that the proposal for the removal of surcharge would mean loss of revenue of about Rs 75,00,000 A small reduction would no doubt have little effect To have the desired result a substantial reduction is necessary Reduction in the freights and abolition of the surcharge, coupled with an increase in the present duty of 10as on foreign coal, should be such as to equalise prices of foreign and Indian coal in all parts of the country Special inducements may also be given to industrial establishments by reducing pro-rata freight and cess on inferior coal

The threat of electricity and other cheaper substitutes make some people apprehend that the demand for coal will be substantially reduced in future. Against this we can view with confidence a still greater increase in the demand for coal, possibly outstripping supply, in the coming days of progressive industrial activities in India Coal is destined to have a bigger market not only as a fuel but as an important raw material for various synthetic products and for its numerous by-products of no less importance.

(d) *The problem of conservation*

The problem of conserving the coal, particularly the resources in good quality coal, has of late become very prominent in the country on account of the interest taken by the Government, the public and the subsequent passing of the Coal Mines Safety (Stowing) Act The question of conservation first came to attract the attention of the Government when Mr R R Simpson, the late Chief Inspector of Mines in India, declared in his presidential speech as President of the Mining and Geological Institute of India that coking coal of good quality in India would last only for 45 years The Government of India were upset by this alarming statement of Mr Simpson and they requisitioned the services of Mr Treharne Rees, a coal expert, who was to report on the most economical extraction and conservation of coal The next to undertake estimates of the probable reserve of coal in India were Dr Sir Lewis Fermor and Dr C S Fox, both of the Geological Survey Dr Fox estimated that at the end of 1932, the total reserves of coal in India were 60,000 million tons of which only 20,000 million tons could be worked Following Dr Fox, the Coal Mining Committee (1937) arrived at the conclusion that at the end of 1936 the reserves of good quality coal were 4889·1 million tons of which only 1426·2 million tons were good quality coking coal The Committee further concluded that the reserves of good quality coal and coking coal, up to the end of 1936, would last 122 years and 62 years respectively. As for Jharia coal the Committee made a more disappointing estimate in that good quality coal and coking coal of that field would last only 81 years and 57 years respectively. Considering the vital importance of coal the statements no doubt arouse grave apprehension But it should be realised that India is a vast subcontinent-like country and a comprehensive geological survey has not been undertaken. The Coal Mining Committee also held the view that the reserves of coal of inferior quality in India were practically unlimited. But these arguments are not meant to minimise the necessity of conservation.

Conservation, broadly understood, implies prevention of avoidable waste of coal through improved methods of mining, making for maximum extraction consistent with safety It also includes utilisation of the different grades for appropriate purposes leading to maximum satisfaction for each variety

Methods of extraction have nowhere come to perfection The Coal Mining Committee cited the case of the United States of America Here in 1921 the average waste was as high as 34 8 per cent The average rate of waste in India, according to the committee, is to the extent of 50 per cent with a tendency to increase As a zealous guardian of the nation's interests the Committee recommended compulsory stowing in the Coal Mines, which the Committee hoped would prevent 40 per cent of the avoidable waste, leaving 10 per cent waste as beyond control

Legal enforcement of compulsory stowing is the first of its kind in India The measure would certainly involve collieries, particularly those producing inferior coal, in incalculable hardship A proposal of this nature it is understood is still under consideration at Geneva As would be expected, the recommendations of the Coal Mining Committee and the Stowing Bill as well, while it was being discussed in the Central Assembly, evoked strong criticism from different quarters

Conservation through the best possible utilisation of the different grades of coal depends largely on extensive research and investigation into their physical and chemical properties So far there is no evidence of any effort in this direction and the indiscriminate use of all grades of coal, resulting in heavy loss, is going on Only about two per cent of the entire coal resources of India belong to the Coking Coal variety The remaining 98 per cent are non-coking and low grade coal, of which only 10% constitute quality coal Superior quality coal from which hard coke is manufactured for metallurgical purposes is indiscriminately used for steam raising in locomotives and power houses. Instances of similar misuse can be multiplied The need of the hour is to encourage study and research for finding profitable uses of superior as well as inferior coal as fuel, raw materials and sources of numerous by-products.

As for research and investigation, it is the Government who should take the lead, because the responsibility is primarily its own Universities and selected Technical Institutions may do useful work in this line. The Coal Mining Committee recommended the establishment of a Coal Research Board The duty of the Board should be more comprehensive and I suggest the formation of an Indian Fuel Research Board which should be entrusted with carrying research into the entire fuel resources of the country Great Britain, Germany, Russia and the United States of America have already such Boards functioning within their borders Great Britain spends nearly one hundred thousand pounds a year and the United States of America spends four to five hundred thousand dollars for the purpose Let us hope that the wheels of Government will move in this direction.

REORGANISATION OF THE INDIAN COAL INDUSTRY

By J K DHOLAKIA,* *M.I Min.E*

The figures of consumption of coal in various Industries in India as estimated and published in the 'Indian Coal Statistics, 1937', are as follows —

	Estimated Consumption.	Per cent of Total.
	Tons	
Railways .	7,934,000	32·9
Admiralty and Royal Indian Marine Shipping accounts .	31,000	0·1
Bunker Coal . . .	840,000	3·5
Cotton Mills .	1,704,000	7·1
Jute Mills .. .	765,000	3·2
Iron, steel and brass foundries (including engineering workshops)	5,984,000	24·8
Port Trust	116,000	0·5
Inland steamers . ..	484,000	2·0
Brick and tile factories (including potteries and Cement works) .	940,000	3·9
Tea gardens	181,000	0·7
Paper Mills . . .	188,000	0·8
Consumption at collieries and wastage	1,277,000	5·3
Balance available for consumption in other industries and for domestic consumption ..	3,661,000	15·2
TOTAL ..	24,105,000	100·0

This will show at a glance what headway the industrial progress of the country has made. It may be made clear that the Bombay Mills are almost entirely on hydro-electric power and there are certain other industries which consume oil fuel including a portion of the North-Western Railway which uses oil fuel in some of its locomotives and another Railway using wood fuel. The equivalence in coal for these two Railways are estimated in the above figures.

The coal resources of the country are of prime importance. The coal industry is the basis of all industries. India takes a second place in the British Empire and ninth in the world for its coal output. The coalfields

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* Balihari Colliery, Manbhum.

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found in Assam have added to our known National Wealth We have coals of different grades, caking and non-caking and high grade and low grade

The iron and steel industry requires hard coke and our supplies of caking coals for this purpose are limited It is therefore to the interest of the nation that such high quality coal should be conserved, but it is a matter for consideration how these coals can be conserved for future generations The Railways, the Mills, the Shippers—all draw mostly from this variety of coal. Efforts are to be made to utilise low grade coal, wherever possible, and conserve this high grade variety for metallurgical purposes

Waste in the working of coal, or any mineral, has to be avoided and steps are being taken to minimise the waste in this industry in the methods of working and to obtain the maximum percentage of extraction from seams by legislation, and stowing is advocated to fill the cavities or hollows from which the coal is extracted and give stability to the surface The problem of supply of stowing materials has yet to be solved The Stowing Board is appointed for the purpose and it is desirable that a larger number of mines should profit by its operation

In addition to hard coke made in modern coke-ovens by which gas is collected and by-products obtained, there are ovens of open types or beehive type in which hard coke is manufactured and all the by-products are run to waste

Further, soft coke, our domestic fuel, is manufactured in open heaps and all the rich volatiles are allowed to waste We have in 1937 manufactured about 850,000 tons of soft coke which means a very great loss of valuable by-products such as motor spirit, light oils, fuel and lubricating oils, carbolic acid, creosote oil, ammonium sulphate, residual pitch and enormous quantities of gas, capable of generating millions of horse power

Research is to be carried out for obtaining smokeless fuel for household purposes and for utilising coal having in its raw state a limited market The Soft Coke Cess Committee is paying a small contribution to the Indian School of Mines, but the results of practical tests, if any, are yet to be published The research needs to be carried out on an extensive scale and on practical utility Smokeless fuel to which attention is being directed in Great Britain is the product of low temperature carbonisation process and it is a fact that the success or failure of such a process is entirely dependent on a market for solid fuel. Attention was also directed to the liquid fuel derived from carbonisation of coal at low temperature and the activities of the financiers who have persistently laid stress on the political value of by-products have been largely responsible for the losses which the public have suffered from investments on unproved processes It is therefore necessary that extensive tests on the technical features of the low Temperature Carbonisation plants have to be carried out and their commercial utility proved.

It has long been recognised that since coal, particularly when coked, is a bad conductor of heat, uniform coking of a charge at low temperature is an entirely different problem from that in high temperature ovens, where nearly all the volatiles are driven off A number of experiments are to be carried out to show whether, under suitable conditions, it is possible to make a good domestic fuel from the extensive supplies of non-coking coals The tests should also be carried out with blendings of different qualities of coal and coke breeze

If a serious attempt is made in this direction, unmarketable low grade coal and some old heaps of coal will be utilised in producing smokeless fuel. The research work, therefore, on Indian coals is highly necessary and special attention has to be directed towards this all important national problem The waste gases liberated and collected can be made useful in running power plants to supply electrical energy to collieries and industries in the vicinity.

Research work in all directions is necessary and a beginning on a very large scale should be made in the search for various coals and the suitability of different grades of coal for different purposes should be established Special attention has to be given to smokeless fuel to be made from grades of coal that appear unmarketable, and tests have to be carried out with different types of ovens to suit the various varieties of coals, their blendings or mixtures even with breeze, as to the possibilities of making briquets which may even be burnt in locomotives, instead of burning high grade coal The recovery of by-products and utilisation of waste gas should also form a part of the research

The coal trade is working under many disabilities If soft coke consumption is popularised, the demand would be very great as fuel and thus the forests will be preserved avoiding the chances of famine and cow-dung can be utilised as manure in the field

If it could be made possible for large scale industries to start and thus utilise the raw materials which are now being exported at ridiculously low prices, the demand would increase in that direction You have noticed that the iron industry alone is taking 25% of the coal output

The Railways in India are not like those in America or other countries where two rival Railways catering for greater comforts always advertise and carry goods and passengers at competitive low rates, but in India the rates of Railway fares and carriage of coal, rather than help the industry's expansion in far off markets, retard the progress and keep it in a moribund condition On the top of this, the coal will not be carried when required during the winter months and collieries have to build up heavy stocks

Furthermore, the Railways increase their output when prices tend to rise and decrease their output when prices come down This state of affairs can be remedied if the Railways purchase all their requirements from the public and keep their coal in reserve for future use, the custom being distributed on as liberal a scale as possible

While considering the amelioration of the coal industry, the question arises as to how to improve the coal trade The simple reply would be that the coal should fetch such a price as would enable the industry to stand on its own feet, permitting it to do what is required for the safety of persons, safety of undertaking and properly organised development The immediate solution would be for the Railways to buy all their requirements from the market, and conserve the coal in their own collieries Owners of mines in the iron and steel industry should draw coal from the public and conserve their coal for future requirements In order to popularise soft coke, intensive propaganda has to be made. Improved quality of soft coke should only be allowed to be despatched and the soft coke made from rejections and pickings should be stopped Unless and until soft coke made from coal that has no market is manufactured, after picking out impurities and shales, and the supplies of clean domestic fuel are assured, no rapid advancement can be made Only if soft coke is popularised as fuel, and if a liberal reduction in Railway freight for smokeless fuel for domestic purposes is made, would the consumption increase greatly and remunerative prices come to stay The Soft Coke Cess Committee has been functioning for some years and the improvements in this direction should engage their serious attention Considering the population of India, if intensive efforts are made in this direction and good quality soft coke is supplied and Railway freight liberally reduced, there is no reason why there should be any over-production

The iron industry has been started on a very large scale only since three decades and is consuming 25% of the coal output When this expands and when other industries grow, there will surely be set up a very good demand for coal. In other countries coal and iron industries flourished side by side and expansion in both the industries went together and the prosperity of the country was the result There is however another view that the prices and output should be controlled. Rationalisation of industry should be attempted and the trial given three to five years. The industry approached the Government of India for such a step in 1934 but with no success. It is hoped that the Government of India will now seriously consider the situation again, and help the coal owners in their efforts to rehabilitate the coal industry by giving them a sympathetic hearing and by allowing the industry to try to shape its destiny for an experimental period of three to five years.

THE PRESENT STATUS OF THE COAL INDUSTRY

By D D THACKER, RAO BAHADUR, *F R S.A* (*Lond*), *M I M.E.*[*]

Coal is an indispensable commodity in modern industrial life being, in fact, the corner stone on which rests the mighty structure of modern industrial development It is a basic industry and is also called a key-industry, as it holds the key to other industries Coal will, therefore, play an important part in any scheme of industrial planning for the country and it augurs well for the future of the coal industry in India that the matter has attracted the serious attention of the Government and of industrial experts who have applied their minds to devise ways and means to prevent waste of this national asset

Compared to the coal mining industry in other countries, the coal mining industry in India is one of recent growth and its development and expansion on modern scientific lines can be said to have commenced only about half a century ago The lack of proper transport facilities was one of the main hindrances to the development of the coal industry in the earlier part of the 19th century when some attempts were made at mining coal in the Bengal coalfield near about Raneegunge The existence of coal has been known to the people of the country since ancient times and as has been observed by the authors of the 'Report of the Indian Coal Mining Committee of 1937' 'Names of villages and localities as Kalipahari (black hill), Damodar (fire in womb), Barakar (big mine) and Angarpathra (charcoal stone) indicate that in olden times coal was used for fuel and reducing iron ore'

The history of the coal industry in India dates from the year 1774 when Messrs Sumner and Suetonius Grant Heatly (who was at the time the Collector of Chotanagpur) obtained permission from the Government to work coal mines in an extensive area near Sitarampur in Bengal There were no facilities for Railway transport in those days and 2,500 maunds of coal that was worked in these mines were transported to Calcutta by river in 1775 Eventually the whole project had to be abandoned and the first venture in coal proved to be an unsuccessful one

Forty years later in 1814, when the Marquis of Hastings was the Governor-General of India, the Government deputed Mr Rupert Jones, a mining expert from England to prospect and report upon the Bengal coalfields With financial help from the Government, he began mining operation in a village near Raneegunge and this undertaking was subsequently taken up in 1835 by Messrs. Alexander & Co., a Calcutta firm and subsequently by Messrs. Carr,

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[*] Pure Jharia Colliery, Manbhum.

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Tagore & Co of which the late Dwarkanath Tagore, the grandfather of our illustrious countryman and poet Dr Rabindranath Tagore, was a partner.

By this time another company, Messrs Jessop & Co, had stepped into the field and opened coal mines at Damulia and Narainpur and worked there up till 1839 when they were transferred to Messrs Gilmore Humfray & Co In 1843 by amalgamating the two firms of Gilmore & Co and Carr, Tagore & Co, Messrs Bengal Coal Company who still own and work a very large number of coal mines in the Raneegunge and Jharia coalfields, came into existence Messrs Bengal Coal Co may thus be regarded as one of the pioneers in the Indian coal industry and they form the link between the old and the new workers in the field Then chronologically we come to the Giridih field where in 1871 the East Indian Railway acquired extensive coal land and opened mines which are being still worked

Though coal mining operations were first started in the Raneegunge field and actual mining operations in the Jharia field commenced as late as 1890, the Jharia coalfield gradually acquired its position of special importance and it now accounts for three-fourths of the total output of coal from the Provinces of Bihar and Orissa.

The Jharia coalfield covers an area of about 180 sq miles in extent lying within the district of Manbhum in Bihar On its western border the Jharia field practically joins on to the Bokaro-Ramgarh field in the Hazaribagh district where the Railways have been working their own mines since 1915

The existence of rich deposits of coal in the Jharia coalfield was known as early as 1839 and an attempt was made to obtain a lease for mining coal within Jharia State in 1858, but the Court of Wards which was then in charge of the State did not grant any lease. The creation of the Department of the Geological Survey of India by the Government and the geological survey of the Jharia coalfield by experts like Mr T W H Hughes in 1866 and by Dr. V. Ball in 1887 and Mr T H Ward in 1890 gradually drew the attention of enterprising businessmen to the prospect of coal industry in the Jharia field, and also impressed upon the East Indian Railway the necessity of extending their branch lines from Barakar to Katrasgarh in 1894 and from Kusunda to Patherdih in 1895, in order to facilitate the development and expansion of coal industry, as without transport facilities it is absolutely impossible for the industry to make any headway.

Though in recent years there has been a very brisk development of the coal mining industry in the Central Provinces and some other places in India, yet the Raneegunge and Jharia fields have still retained their positions of importance and in 1935 the Jharia and Raneegunge coalfields accounted for 78·96% of the total output. It will be interesting to note here that the yield of the Jharia and Raneegunge fields in relation to the total Indian output has been climbing down since 1920, it being 83·67% of the total in 1920, 84·76% in 1923, 79·23% in 1930 and 78·96% in 1935.

The early methods that were adopted for mining coal were comparatively simple and coal was raised gradually by working quarries at shallow depths and later galleries were driven from the quarries and work was mostly carried out in the daytime and night work was only introduced still later

With the expansion of Railways and better transport facilities, better and improved methods of mining were undertaken by enterprising businessmen and mining gradually became a more difficult and hazardous job

The enactment of the Indian Mines Act in 1901, which provided for better and more scientific methods of working under properly qualified and trained colliery managers, marked a new epoch in the history of the mining industry in this country and ensured better safety for workers and more methodical working under the supervision and control of a Government Inspectorate headed by a Chief Inspector of Mines The office of the Chief Inspector of Mines was at first located at Calcutta where it remained until 1907 when it was removed to Dhanbad, so that better and more effective control could be exercised over the coal mines which have been daily increasing in number round about the Jharia coalfield

As workings became old and depillaring operations were sought to be carried out, and the chances of accidents and collapses and of fires in mines increased, considerable amendments have been effected in recent years in the Indian Mines Act and in the various Rules and Regulations framed thereunder to minimise the chances of such accidents The recent enactment of provisions for compulsory stowing of deep mines and of setting up of two Rescue Stations, one in the Jharia field and another in the Raneegunge field, are attempts to check the growing evil of underground accidents by subsidence and fire

I do not think, in speaking about the present status of the coal industry, I should allow myself to drift away into the details of the various legislative measures that have been enacted in recent years to ensure and provide for the better safety of workers, adoption of better and more improved methods of mining and other ameliorative measures for the welfare of labour and compensation to workers in case of accidents All that I need say is that they have to a certain extent added to our cost of production and when we take into consideration the Provincial enactments such as the Bihar and Orissa Mining Settlement Act or the Bengal Mining Settlement Act or the Jharia Water Supply Act or the Amended Road Cess Act, the burden that has been thrown upon the industry will appear by no means to be inconsiderable

As I have already stated, the two coalfields of major importance are the Raneegunge and the Jharia coalfields though, in recent years, in spite of the comparative inferiority of its coal, the Central Provinces has, because of its geographical position, turned out to be a formidable rival of Bengal and Bihar coal in the important coal-consuming centres of Western India, such as Bombay and Ahmedabad

The broad difference between Raneegunge and Jharia coal is that, while Jharia coal is caking coal, the Raneegunge coal is mostly non-caking or partially caking. Raneegunge coal is richer in volatile matter and because of its low volatile matter Jharia coal gives better results in an ordinary locomotive boiler, but Raneegunge and Jharia coal each has its own use and is good for its own purpose

The important position that the coal industry occupies today was not attained in a day I have attempted to give you a very brief outline of its struggles during the early years of the 19th century when some pioneer attempts had failed, because of transport and other difficulties and the predilection of the consumers, who were also then very few and in favour of the superior quality of imported *Walesh* coal

The history of the present coal industry therefore really dates from the beginning of the 20th century and a mere glance at the annual figures of the output of coal during the last 40 years will show how rapid has been the development According to the Report of the Coal Mining Committee, between 1880 and 1919 the production of coal in India doubled every 10 years The reason which led to this phenomenal growth of the coal industry during these years were —

(i) Development in the export trade of coal
(ii) The expansion of Railways which are the biggest consumers of coal at present
(iii) The development of iron and steel industry which is the second big consumer next to the Railways
(iv) The establishment of cotton, jute and other mills
(v) The development of other various industries and factories and
(vi) The last, though not least, an increased use of coal as domestic fuel, in the shape of soft coke

In comparison to the vast size of the Indian population, the figure of coal used for domestic consumption at present is almost negligible There is a very great potential market for low grade coal of the country in the domestic hearth of India's teeming millions and if this market can be properly tapped I am sure it will go a great way to remove the hardship under which many second class collieries are labouring at present The work that is being done by the Soft Coke Cess Committee for popularising the use of soft coke as domestic fuel has to a certain extent stimulated the internal demand for domestic coal and the possibilities that lie ahead are still very great. It may be interesting to note here the approximate figures of coal consumed by the various industries during the year 1936

	Tons.
Railways	7,482,000
Iron and steel industries	6,681,000
Other industrial and domestic consumption	2,759,000
Cotton mills	1,697,000
Bunker coal	990,000
Brick manufacture	858,000
Jute mills	745,000

	Tons.
Inland steamers	567,000
Tea and paper industries	379,000

Though the Railways have been and are still the biggest consumers of coal, yet the development of their own collieries by the Railways has adversely affected the general trade due to the loss of a considerable portion of the Railway custom

The exports of Indian coal to foreign countries began to increase gradually from the beginning of the present century and from an annual average figure of 305,000 tons prior to 1900, it reached the figure of 1,224,758 tons in 1920 which was the highest ever recorded

The chief places of export outside India were Colombo, Singapore, Penang, Sabang, Rangoon and some other places, while coal was exported coastwise to inland ports like Madras, Bombay and Karachi

Closely following on the Great War and taking advantage of the immobile position of the trade due to scarcity in the supply of Railway wagons for transport of coal, consequent on the greater demand for Railway wagons for other trades and industries, two formidable rivals in the shape of Welsh and Natal coal appeared in the important coal-consuming centres of Western India. The Welsh coal could compete favourably because of its superior quality, while the South African coal was placed in a position of advantage because of the bounty it received from the South African Government by way of rebate in shipping freight Though the cost of production of Indian coal is very low in comparison to the cost of production in the other countries, yet the exorbitant railway freight on Indian coal made it possible for sea-borne foreign coal to oust successfully the Indian coal from some of its paying internal markets While faced on the one hand with this keen competition with foreign coal in the internal markets, the Bengal and Bihar coal had also to reckon with the competition from C.P. coal, because of the special advantage enjoyed by it owing to its proximity to coal-consuming centres like Bombay and Ahmedabad and the consequent cheapness in Railway freight On top of this came the embargo that was placed by the Government of India in 1920 on the export of Indian coal to foreign countries with the result that the Indian coal trade in overseas markets was completely lost The position of the Indian coal trade became so very critical in or about this time that it shook the attitude of the stolid indifference taken up so long by the public and the government In March 1924 the Indian Legislative Assembly recommended to the Tariff Board the investigation into the question of offering some protection to the Indian coal trade against foreign competition. The result was the subsequent imposition of a countervailing duty of annas eight per ton on all foreign coals imported into India But as was expected, the relief was extremely inadequate

In the very same year, *i.e* September 1924, the Government of India appointed an expert committee under the chairmanship of Sir Frank Noyce to enquire and report on measures to stimulate the export of Indian coal to Indian and foreign ports and in particular to see what effective measures could be taken for pooling and grading Indian coal for export and bunkering. The Noyce Committee carried out a thorough investigation into the matter and on the recommendation of that Committee the Indian Coal Grading Board was constituted and the Coal Grading Act was passed providing for certification of coal intended for export

The Indian Coal Grading Board under the able guidance of the Chief Mining Engineer to the Railway Board, who is the Chairman of the Board, and his Inspection Staff, both on the collieries and at the Kidderpore Docks, are doing valuable work Through the efforts of the Board Indian coal has been able to win back much of the confidence that it had lost in the foreign markets and has been able to retrieve partially its position in those places

The export trade has considerably improved during recent years In 1937, the total shipment of Indian coal to various Indian and Chinese ports was over 1½ million tons In 1938, there was a heavy demand for coal from China and the total export figure reached 2,210,130 tons as against the annual average of 3,28,000 tons for the previous five years

The output of Indian coal has been rising higher and higher every year and the year 1937 was perhaps the peak year with a total figure of over 25 million tons But this rise in output is no index to the prosperity of the trade and has been, on the contrary, one of its sources of weakness as it has led to keen internal competition and suicidal cutting down of prices below the actual cost of production

Overproduction has been characterised by some as a special disease of the Indian coal trade I cannot do better than quote in this connection the observations of the Coal Mining Committee —

> 'Economic science says that "supply price" is cost of production plus a reasonable profit, but there seems little or no margin of profit in prices which most coal of good quality has been fetching during the past few years These low prices are due to interaction of keen competition and decreased demand due to general depression Potential production exceeds demand and competition compels the quotation of prices based on potential rather than actual production '

The truth of these observations will be apparent from the fact that during the last five years the average selling price of first class or selected grade coal was Rs 3-12-0, Rs.3-4-0, Rs 3-2-0, Rs 5-8-0 and Rs 5-0-0 per ton, for colliery siding, while average raising cost comes to over Rs 5-0-0 per ton

The Indian coal industry stands at present faced with a variety of problems the chief amongst which are the better utilisation of the low grade coal, (2) prevention of the present wasteful methods of working, (3) the recovery of the by-products of coal, and (4) conservation of the caking coal for metallurgical purposes

CHEMICAL CONSTITUTION OF COAL

By N N CHATTERJEE *

In order to understand the nature of the coal constituents chemists followed various methods which may be classified under three principal heads —

(i) Chemical attack by means of various reagents which oxidise, decompose or otherwise alter the coal substance

(ii) The action of various organic solvents which are supposed to extract fractionally certain constituents without radically altering them.

(iii) The action of heat on the original coal or of some extracted portions at certain definite temperature and the examination of the products so obtained This includes the process of coal distillation and the examination of various distillates

Regarding the first method the reagents chiefly employed have been sulphuric acid, nitric acid, caustic alkalies, bromine, ozone, oxygen, etc. Coal being a heterogeneous mixture of several complex compounds most of which are imperfectly soluble in any known reagents The scientists made attempts to transform some of them by various chemical treatment into simpler definite products capable of further investigation and identification Such attempts, however, have been unsuccessful because by such treatment the yields were either too small or the products were themselves in an advanced stage of decomposition, thereby giving no clue as to the real nature of the organic compounds originally present in the coal substance

Regarding the third method the coal is subjected to destructive distillation and the various coal constituents are decomposed at different temperatures and give rise to various chemical compounds of different thermal stability In this process also the resultant chemical compounds do not enlighten us in the matter of obtaining definite information as to the real nature of the compounds originally present in coal

The second process of attacking the coal by various organic solvents is undoubtedly preferable to either of the above two processes because it enables us to extract some portions, if not all, of the various constituents of coal with minimum alteration or decomposition of the coal substance The difficulty is in the selection of a proper solvent that will behave differently to the different coal constituents and at the same time will be able to extract a large proportion of them without destroying the whole structure

By suitable solvents and by following proper technique and at the same time avoiding any decomposition of the coal substance this process has been

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* Department of Geology, Calcutta University.

VOL. VI—No. 3 [Published August 22nd, 1940.

found to separate various compounds from coal and by careful investigation the definite chemical nature of them has been studied and established

Already a considerable amount of work has been done with regard to the action of various organic solvents on coal substance in order to elucidate the nature of the constituents present in it The principle underlying the solvent action is to break up the coal substance into different fractions without materially decomposing it Various organic solvents such as benzene, chloroform, ethyl ether, ethyl alcohol, light petroleum, acetone, aniline, quinolene, phenol, etc , were employed with varied results In 1899 Bedson found that pyridine has a remarkable solvent action upon coals and subsequently pyridine as a suitable solvent came into general use It will be out of place here to give a detailed account of this solvent work carried out by various scientists in different countries The author of this note carried out some work in this line and followed Prof Wheeler in selecting pyridine and chloroform as the most suitable solvents for extraction purposes Of the recent works in this line mention should also be made of the researches carried out by Bone and Illingworth. Prof Bone constructed an apparatus which operates on the automatic soxhlet principle under pressure up to 700 lb per sq. in by which means he could extract a greater quantity in a shorter period The solvent used by him was benzene Illingworth carried out investigations in this direction and observed that by heating the coal at 200°C for 24 hours out of contact with air the rate at which the extraction proceeded was much increased But when extracted for a long period the amount of extract was practically the same under both conditions From his experience it was found that slightly greater extraction was possible with chloroform than with benzene Parr and Hadley carried on some extraction with phenol at 100°C for 20 hours in an atmosphere of CO_2 By such treatment they could eliminate resinic organic sulphur from coal Fischer and Gluud studied the action of benzene upon coals at 288°C and about 50 atmospheres

It may be mentioned that very little work has hitherto been done to find out the effect of solvents on Indian coals. Carrick Anderson and Henderson followed the method of Bedson and carried out some experiments with Bengal and Japan coals. They used commercial pyridine as the solvent, boiling at 110–120°C. in soxhlet apparatus It has been pointed out by Illingworth that though better extraction is possible with phenol at higher temperature (400°C), yet at temperatures under 120°C the pyridine has been found to be more efficacious in its action. It was suggested by Bone and Wheeler that at higher temperature, sometimes as low as 180°C , there was a chance that there might ensue some decomposition in the coal substance. The author of this paper has done some work in this line and carried out soxhlet extractions with pyridine and chloroform as suitable solvents and did not therefore prefer to experiment at higher temperatures. The details of the technique followed in the laboratory have already been published.[1] The coals that were subjected to laboratory investigation included the Tertiary coals of Assam and N W India and some specimens of Gondwana coals The author of this paper takes this opportunity of expressing his best thanks to Dr Fox for kindly giving him some specimens of Tertiary coals for investigation

When coal is subjected to the action of pyridine in the soxhlet apparatus it splits up into insoluble (alpha cellulosic coal or alpha compound) and soluble (beta cellulosic and gamma resinic substance) portions The soluble portion (beta and gamma compounds) on further treatment with chloroform in the soxhlet apparatus is found to break up into insoluble (beta compound) and soluble (gamma compound) fractions The coal substance thus resolves into cellulosic and resinic components The chemical nature and other different properties of these substances have been carefully studied and established and it will be out of place here to enter into those details The respective amounts of these compounds present in the different coal specimens of India have been determined quantitatively and the results are enumerated in Table II Table I gives the proximate analyses of the coal specimens The method adopted for proximate analyses has been described in a previous communication [2] Table III gives the ultimate analyses of these coals In the following lines a discussion is given of the presence of these chemical constituents and their relation with caking and swelling properties of the coals

The alpha, beta and gamma compounds have been separately examined and their behaviour under heat treatment studied The alpha compounds obtained from all the specimens of caking coals do not show any tendency to form a coherent mass when subjected to destructive distillation In other words it may be said that the caking property of a coal is almost entirely destroyed by the leaching action of pyridine on the coal substance The beta compounds obtained by the action of pyridine and chloroform on the coal specimens, when strongly heated in a covered platinum crucible, are found to give rise to a swelled mass though the particles are not held together very firmly The gamma compound on being heated generally liquates and melts at a much lower temperature and is found to yield the cementing substance which binds together the other coal particles When further heated at higher temperature it forms a swelled mass. A mixture of alpha cellulosic coal particles and gamma compounds in definite proportions when heated is found to produce a coherent mass. The beta compound is also able to take up some amount of alpha cellulosic particles to form a swelled mass when subjected to process of carbonisation It is also found that a mixture of alpha, beta and gamma compounds in the same proportion as present in the coal substance produces a good coke though slightly inferior to the coke obtained from the coal.

Two specimens of caking coal (seams Nos XIV and XV) were heated for several hours at 105°C -110°C in presence of air and the caking property eventually destroyed These specimens were then subjected to the action of pyridine and chloroform and the results of these experiments are given below,—

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Already a considerable amount of work has been done with regard to the action of various organic solvents on coal substance in order to elucidate the nature of the constituents present in it The principle underlying the solvent action is to break up the coal substance into different fractions without materially decomposing it Various organic solvents such as benzene, chloroform, ethyl ether, ethyl alcohol, light petroleum, acetone, aniline, quinolene, phenol, etc , were employed with varied results In 1899 Bedson found that pyridine has a remarkable solvent action upon coals and subsequently pyridine as a suitable solvent came into general use It will be out of place here to give a detailed account of this solvent work carried out by various scientists in different countries The author of this note carried out some work in this line and followed Prof Wheeler in selecting pyridine and chloroform as the most suitable solvents for extraction purposes Of the recent works in this line mention should also be made of the researches carried out by Bone and Illingworth Prof Bone constructed an apparatus which operates on the automatic soxhlet principle under pressure up to 700 lb per sq in by which means he could extract a greater quantity in a shorter period The solvent used by him was benzene Illingworth carried out investigations in this direction and observed that by heating the coal at 200°C for 24 hours out of contact with air the rate at which the extraction proceeded was much increased But when extracted for a long period the amount of extract was practically the same under both conditions From his experience it was found that slightly greater extraction was possible with chloroform than with benzene Parr and Hadley carried on some extraction with phenol at 100°C for 20 hours in an atmosphere of CO_2 By such treatment they could eliminate resinic organic sulphur from coal Fischer and Gluud studied the action of benzene upon coals at 288°C and about 50 atmospheres

It may be mentioned that very little work has hitherto been done to find out the effect of solvents on Indian coals Carrick Anderson and Henderson followed the method of Bedson and carried out some experiments with Bengal and Japan coals They used commercial pyridine as the solvent, boiling at 110–120°C. in soxhlet apparatus. It has been pointed out by Illingworth that though better extraction is possible with phenol at higher temperature (400°C), yet at temperatures under 120°C the pyridine has been found to be more efficacious in its action It was suggested by Bone and Wheeler that at higher temperature, sometimes as low as 180°C , there was a chance that there might ensue some decomposition in the coal substance The author of this paper has done some work in this line and carried out soxhlet extractions with pyridine and chloroform as suitable solvents and did not therefore prefer to experiment at higher temperatures The details of the technique followed in the laboratory have already been published [1] The coals that were subjected to laboratory investigation included the Tertiary coals of Assam and N W India and some specimens of Gondwana coals The author of this paper takes this opportunity of expressing his best thanks to Dr Fox for kindly giving him some specimens of Tertiary coals for investigation

When coal is subjected to the action of pyridine in the soxhlet apparatus it splits up into insoluble (alpha cellulosic coal or alpha compound) and soluble (beta cellulosic and gamma resinic substance) portions The soluble portion (beta and gamma compounds) on further treatment with chloroform in the soxhlet apparatus is found to break up into insoluble (beta compound) and soluble (gamma compound) fractions The coal substance thus resolves into cellulosic and resinic components The chemical nature and other different properties of those substances have been carefully studied and established and it will be out of place here to enter into those details The respective amounts of these compounds present in the different coal specimens of India have been determined quantitatively and the results are enumerated in Table II Table I gives the proximate analyses of the coal specimens The method adopted for proximate analyses has been described in a previous communication [2] Table III gives the ultimate analyses of these coals In the following lines a discussion is given of the presence of these chemical constituents and their relation with caking and swelling properties of the coals

The alpha, beta and gamma compounds have been separately examined and their behaviour under heat treatment studied The alpha compounds obtained from all the specimens of caking coals do not show any tendency to form a coherent mass when subjected to destructive distillation In other words it may be said that the caking property of a coal is almost entirely destroyed by the leaching action of pyridine on the coal substance The beta compounds obtained by the action of pyridine and chloroform on the coal specimens, when strongly heated in a covered platinum crucible, are found to give rise to a swelled mass though the particles are not held together very firmly The gamma compound on being heated generally liquates and melts at a much lower temperature and is found to yield the cementing substance which binds together the other coal particles When further heated at higher temperature it forms a swelled mass. A mixture of alpha cellulosic coal particles and gamma compounds in definite proportions when heated is found to produce a coherent mass The beta compound is also able to take up some amount of alpha cellulosic particles to form a swelled mass when subjected to process of carbonisation. It is also found that a mixture of alpha, beta and gamma compounds in the same proportion as present in the coal substance produces a good coke though slightly inferior to the coke obtained from the coal

Two specimens of caking coal (seams Nos XIV and XV) were heated for several hours at 105°C-110°C in presence of air and the caking property eventually destroyed. These specimens were then subjected to the action of pyridine and chloroform and the results of these experiments are given below:—

(Coal oxidised at 105°C -110°C and caking property destroyed)

%	Seam XIV.	Seam XV
Alpha compound (α)	93·00	84·02
Beta compound (β)	0·50	6·70
Gamma compound (γ)	6·50	9·28
Total pyridine extract ($\beta+\gamma$)	7·00	15·98

Untreated coal

%	Seam XIV	Seam XV
Alpha compound (α)	93·43	84·32
Beta compound (β)	0·20	6·68
Gamma compound (γ)	6·37	9·00
Total pyridine extract ($\beta+\gamma$)	6·57	15·68

DISCUSSION OF RESULTS.

It will be out of place here to enumerate in detail the views held by previous workers on this subject as an excellent historical summary has been published by Bakos[3] It may be mentioned that Prof Wheeler and his school carried out extractions of coal with pyridine and chloroform and a comprehensive work on the extraction with benzene under pressure was carried out by Fischer and Bone and their associates Illingworth also conducted experiments after Wheeler with pyridine and chloroform and put forward certain generalised statements which require verification Illingworth concludes that for the coals with C/H ratio higher than 10, coke can only be formed when more than 5·5% of gamma compound is present. The gamma content is maximum in coals when C/H ratio is between 17 and 18. An increase of C/H ratio will decrease the gamma content According to him the beta compound is found to occur in greatest amount in coals with C/H ratio between 14 and 15. He also concludes that increase of C/H ratio decreases the beta content of coal

Referring now to the analytical results given in Table II it will be seen that many of the caking coals contain gamma compound more than 5% which go to support partially the views of Illingworth The relationship proposed by him between the pyridine extracts and C/H ratio does not seem to hold good in every case. There are certain exceptions which suggest that the resinic coking theory as put forward by Illingworth should be accepted with reserve. Besides, the results obtained by Foxwell[4] in this direction do not go to support the views of Illingworth in all their entirety.

So far as the caking principle is concerned Cockram and Wheeler[5] conclude that caking property is due to the presence of resins and hydrocarbons contained in the coals or derived from these substances during the early stages of heating Foxwell [6] lays importance on the extrusion of molten matter in the first stage of coking consisting of gamma from the interior of coal He thinks that the coking power of a coal is due not so much to the actual amount of the gamma fraction which it contains as to its mode of extrusion when the coal is heated It may be pointed out that Foxwell obtained a tolerably good coke from a South Welsh coal containing only 0 1% of gamma compound The author of this note also found that the strongly caking Jammu coal contained only 0 37% of gamma and 0 73% of beta compound Foxwell also observed that there are some coals containing a large amount of gamma fraction which do not yield coke A reference to Table II will show that Borjan non-caking coal of upper Assam contains an appreciable amount of beta and gamma compounds Foxwell suggests that some structural peculiarity in the coal may prevent the extrusion of the gamma fraction in the proper manner and that this may be one of the factors responsible for the non-caking nature of such coals

Foxwell lays much stress on the presence of the gamma fraction and does not discuss in detail the nature of the beta fraction and its rôle in the caking and swelling properties The author of the present paper, however, finds that the swelling and caking properties of coal are connected with the presence of both the beta and gamma fractions and not the gamma compound alone Sinnatt's [7] suggestion that the gamma compound alone is responsible for swelling and caking does not seem to tally with the author's experimental observations Beta particles on being heated are found to produce a highly swelled and coherent mass showing clearly that the swelling property of coal is to be ascribed to the presence of the beta compound, a suggestion already made by Shimura [8] and Barash [9] The fact that beautiful cenospheres are obtained by Bakes [10] from beta fraction goes to oppose Sinnatt's view As the beta particles get cemented together during the process of heating it is clear that a certain amount of binding or cementing substance is derived from this compound The analytical results given in the tables accompanying this paper show that there are few exceptions to this statement The three specimens of Raniganj coals (Poniati, Ninga and Ghusick seams) contain a sufficient amount of beta and gamma compounds yet they swell only slightly during caking Following Foxwell's suggestion it may be said that some structural peculiarity in the coal substance may be held partly responsible for this There are reasons to believe that the physical condition of the alpha cellulosic fraction in these specimens has a great influence on the beta and gamma compounds in preventing the formation of a highly swelled and coherent mass.

The coal specimens (seam Nos. XIV and XV) on slow oxidation are found to have lost their caking property The amounts of pyridine extract in these specimens remain more or less the same before and after the oxidation. As suggested by Barash [11] the only explanation that can be given is that by the oxidation of the coal substance at an elevated temperature the physical condition and structural peculiarity of the alpha fraction become altered sufficiently to behave in a different manner than in the untreated coal Similar instances have also been recorded by Barash,[12] the only difference being that Barash kept the coal specimens exposed to air for a considerable length of time instead of heating as in the case of the present author's experiments Barash's suggestion that the alpha compound develops increased absorptive capacity appears to be reasonable

From what has been said and discussed above it appears that the alpha fraction without being an inert substance, as has hitherto been supposed to be, plays an important rôle in the process of carbonisation, details of which have yet to be thoroughly studied

With regard to the gamma content it may be pointed out that almost all the specimens of caking coal included in the present paper contain more than 5% gamma fraction and that all the coals are not equally caking as shown by the different values of their caking indices (Table I) An exceptional case has been recorded This specimen (seam No X), however, contains a slight amount of beta compound which is responsible for the non-swelling nature of this coal A scrutiny of the analytical results given in the tables will show that the gamma fraction is mainly responsible for the development of cementing material in the coal substance. From the behaviour of the gamma fraction during heat treatment it is found that some amount of swelling is also due to the presence of this compound

From what has been said and discussed in the foregoing pages it is clear that the generalised statements put forward by Illingworth and the suggestions made by various other authors regarding the relationship between the pyridine extracts and caking and swelling properties do not appear to be strictly applicable in the case of coal specimens described in this paper

Though the suggestions made by Bakes[13] are in general harmony with the observations recorded in this paper regarding the caking and swelling properties of coal, yet slight modification is necessary as suggested below for the proper explanation of the facts observed by the present author Bakes' conclusion is that during the plastic stage two types of plastic material may be present The first (caking constituent) consists of a dispersion of gamma 2 and gamma 3 in gamma 1 The second type of plastic material (the swelling constituent) results from the fusion of portions of coal similar in nature to the beta fraction which may be obtained by pyridine extraction The author of this paper has already pointed out in the foregoing pages that the beta compound, besides being responsible for the swelling property, also gives rise to some cementing substance and that the gamma fraction when heated liquates at lower temperature and swells to some extent on further heating at higher temperature, showing that gamma is mainly responsible for the development of the cementing material in the coal substance and partially for the swelling It is also evident that caking and swelling properties are the results of a combination of physical and chemical reactions which take place in the coal substance partly simultaneously and partly successively. There are, however, indications that the physical condition and structural peculiarity exert some influence during the caking process and further work is necessary in this direction before any generalised statement can be put forward No definite relationship between C/H ratio and the alpha, beta and gamma fractions has been observed at this stage of investigation.

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TABLE I. (*Proximate Analyses*)

	Jharia Coalfield.					Giri-dih.	Raniganj Coalfield						
%	Seam X	Seam XI	Seam XII	Seam XIV	Seam XV	Ramnadih Colliery	Dishergarh Seam	Poniati Seam	Ninga Seam	Ghusick Seam	Laikdih Vitrain	Laikdih Durain	Borodhemo Fusain
Moisture	1 18	0·60	1 18	1 52	1 26	1·02	2 60	3 24	4 28	5 30	1 96	1 68	2·00
Volatile Matter	17 48	19·92	23·15	20 10	21·96	24·60	30·02	29·32	30·03	32·04	29 75	25 53	20 60
Ash	24 60	18 82	7·08	12 80	13 16	8 54	10 45	11 12	12·00	10·50	4 20	18 08	9 80
Fixed Carbon	56·74	60·66	68 59	65 58	63 62	65 84	56·93	56 32	53·69	52 16	64 10	54 81	67 60
TOTAL	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100 00	100·00
Colour of ash.	Grey	White.	Grey	Faint Pink.	Grey	Pink.	Buff	Grey	Buff	Grey	White	Cream	Pink
Nature of the Coke residue.	Cakes without swelling	Caking and non-swelling	Caking and high swelling	Caking and non-swelling	Caking and swelling	Caking strongly and high-swelling	Caking and swelling	Caking and slightly-swelling	Caking and slightly swelling	Caking and slightly swelling	Strongly-caking and high swelling	Caking and non swelling	Non-caking
Caking Index.	6	6	9	8	10	12	10	8	8	8	12	11	

	Jharia.	Raj-mahal Hills.	Tal chir	Assam			N W India.			Kash-mir
%	Ekra Fusain	Jilbari Fusain	Talchir Fusain	Borjan Coal (resinous)	Namdang Coal	Borjan Coal (non-caking)	Makerwal	Mach.	Dandot (Punjab)	Jammu anthracitic.
Moisture	2 20	8 50	4 20	4 60	2·05	4 88	3 78	10 83	5·09	0 83
Volatile Matter	21 05	35 66	31 29	48 91	41·95	43 82	49 79	40 57	43·41	14 40
Ash	15 85	11 20	5 40	3 03	0 69	2 37	10 00	2 32	12 10	12·11
Fixed Carbon	60 90	44 64	59 11	43 46	55 31	48 93	36 43	46 28	39 40	72·66
TOTAL	100 00	100 00	100 00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Colour of ash.	White	Brown	Brown	Deep Pink	Faint Pink	Cream	Light Pink	Light Red	Brick Red.	Cream.
Nature of the Coke residue.	Non caking	Non caking	Non-caking	Caking and slightly swelling	Strongly caking and swelling	Non caking	Caking	Caking	Caking	Strongly caking
Caking Index.				10	12					

TABLE II. (*Pyridine and Chloroform extracts*)

%	Jharia field					Giridih.	Raniganj							Jharia.	Rajmahal.	Talchir	Assam.			N W India.			Kashmir
	Seam No X.	Seam XI	Seam XII	Seam XIV	Seam XV	Ramnadih Colliery	Dishergarh Seam.	Poniati Seam	Ninga Seam	Ghusick Seam	Laikdih Vitrain	Laikdih Durain	Borodhemo Fusain	Ekra Fusain.	Jilbari Fusain.	Talchir Fusain	Borjan Coal (resinous)	Namdang Coal	Borjan Coal non-caking	Makerwal	Mach.	Dandot (Punjab)	Jammu.
Alpha Compound (α) .	96·00	93 80	87·00	93 45	84 32	69·67	76·09	82 14	85·30	86·00	75·90	83 90	96 80	97·00	96 50	97 00	76 16	79 51	84 30	80·09	83 18	80 72	98 70
Beta Compound (β)	1·43	1·02	4·45	0 20	6·68	17 88	14 13	7 51	8 50	7 50	10·00	4 80	2 00	1 80	2·02	1 72	12 76	8 25	7·00	8 10	8 77	6 42	0·73
Gamma Compound (γ) .	2·57	5·18	8 55	6·37	9·00	12 45	9 78	10·35	6 20	6 50	14 30	11 30	1 20	1 20	1 48	1 28	11 04	12 30	7 35	11 81	8·06	12 84	0 37
Total Pyridine extract ($\beta+\gamma$)	4·00	6 20	13·00	6·57	15·68	30 33	23·91	17 86	14 70	14 00	24 30	16 10	3 20	2 80	3 50	3·00	23 80	20 53	14 35	19·91	16 83	19·26	1 10

TABLE III (*Ultimate Analyses*)

%	Jharia Field.					Giridih.	Raniganj Field.							Jharia.	Raj mahal Hills	Talchir	Assam.		
	Seam X	Seam XI.	Seam XII	Seam XIV	Seam XV	Ramnadih Colliery	Dishergarh Seam.	Poniati Seam	Ninga Seam	Ghusick Seam	Laikdih Vitrain	Laikdih Durain	Borodhemo Fusain.	Ekra Fusain	Jilbari Fusain	Talchir Fusain	Borjan Coal (resinous)	Namdang Coal	Borjan Coal (non-caking)
C	63·60	70 30	75·92	73 69	75 36	78 43	72 10	71 70	68·65	71 13	79 17	65 80	75 79	74 63	69·52	81 22	78·02	79·66	78·43
H .	4·66	4 26	4·98	4·96	5 20	4 70	4 50	4 55	4 72	4 93	5·93	4 34	3·61	3 80	5 12	4·06	5 92	5 84	5 54
O+N .	6·62	5·93	11 22	7 95	5 56	7 80	12 51	12 20	12 41	13·04	10·09	11 34	10·01	10 12	13 71	10 21	9 28	10·80	11 36
S .	0·52	0·67	0·80	0 60	0·72	0·57	0·44	0 53	0·42	0·40	0 61	0 49	0·79	0 60	0 45	0 51	3 75	3·01	2 30
Ash	24·60	18·82	7·08	12 80	13 16	8 50	10·45	11·02	13 80	10·50	4 20	18·03	9·80	10 85	11 20	4·00	3·03	0·69	2 37
TOTAL	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100 00	100·00	100·00
C/H Ratio .	13·6	16·5	15·2	15	14 5	16 7	16	16	14 5	14 5	13 4	15	21	19·6	14	20	13	13·6	14

METHODS OF ANALYSIS OF COAL

ON THE NECESSITY OF STANDARDISING A METHOD FOR THE PROXIMATE ANALYSIS OF COAL IN INDIA

By N N. CHATTERJEE *

The scientific workers in India engaged in coal research are sometimes faced with the problem as to the selection of the best method for carrying out the proximate analysis of coal After the establishment of the Coal Grading Board in 1925 by the India Government the grading of coal on the basis of proximate analysis has been in practice and business transactions are carried out on the production of a certificate from the Coal Grading Board

The Coal Grading Board, however, issues the certificates on getting the analytical report from the laboratory of the Alipur Test House Almost all the coal seams in the important coalfields of Bengal, Bihar and C P. have been graded in this way depending on the analytical results obtained from the said Test House The coal producers and consumers are thus guided in the inland and foreign market by the certificates issued by the Coal Grading Board The scientists working in different laboratories were always under the impression that the method followed by the Alipur Test House must have been a standard one free from inaccuracies Later on in 1930 the method adopted by the Alipur Test House and on which the grading of coal seams is carried out was published by Brodie[1] in the *Records of the Geological Survey of India* The method outlined by Brodie does not appear to be satisfactory and differs from the standard methods of England and America. A discussion of Brodie's method was communicated by the present author to the Geological, Mining and Metallurgical Society of India on the 18th September in the same year[2]

The present author is not aware if any modification or improvement has since then been made in the Alipur Test House method. The writer therefore wants to put forward this discussion on the subject and has made an attempt in the following lines to show the necessity of standardising a method for the proximate analysis of coal in India. The attention of the scientists engaged in coal research in India should be drawn to this part of the problem and the present writer suggests that a standard method should be followed or a suitable method be evolved and standardised for use in the different laboratories of India for obtaining a much better and uniform result.

The method of proximate analysis of coal attracted the attention of the early scientists. It was also realised by them that the percentages of moisture

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[Published August 22nd, 1940.

and volatile matter vary considerably depending on various factors and the methods of analysis. The values obtained by proximate analyses were therefore regarded as more or less arbitrary. Hence the chemists and scientists of different countries evolved some standard methods for the analysis of coal so that people working at different centres in the same country may obtain some concordant results by following one standardised method Thus we have got a few methods as recommended by the United States Bureau of Mines,[3] by the Fuel Research Board of England,[4] the South African Branch of the British Engineering Standard Association,[5] and the United States Steel Corporation [6] But unfortunately in India we do not find any such standard method for proximate analysis of coal With the inception of the Coal Grading Board the utility of representative samples has been realised by everybody and at the present day mine sampling and laboratory sampling are being gradually introduced everywhere. In 1910 Cunningham Hughes [7] published an article on proximate analysis of coal In this paper he made an attempt to put forward a method of analysing coal but as the method was not highly perfect it did not receive much recognition

In the article dealing with the method of Brodie we find that he felt the necessity of one standard method for such analytical work But the author of this note fails to understand why a method was adopted differing greatly from the standard methods recommended by the U S. Bureau of Mines or the British Fuel Research Board. In that paper sufficient reasons have not been given for such deviation.

The method of determination of moisture content in a specimen of coal was discussed in the 8th International Congress of Applied Chemistry in 1912 and it appears from the report [8] that one gram of coal should be heated in a constant temperature oven at 105°C.–107°C. for one hour, then it should be allowed to cool in a desiccator and weighed and the percentage of moisture calculated. A similar method is also recommended by the American Chemical Society [9] and is in general practice in America and other countries.[10] Shallow vessels are used in all cases for the determination of moisture.

In the Alipur Test House method about two grams of powdered coal are weighed in a weighing bottle and heated in an air oven at a temperature of 105°C. until all the moisture has been driven off and a constant weight obtained. This requires about two hours [11] In the description no specification regarding the dimension of the weighing bottle has been made This omission is regrettable. There are several types of weighing bottles, if the bottle be of narrower type a quantity of two grams will form a thick layer in the bottle and it will take a much longer time for the complete evolution of moisture. The writer of the present note has found experimentally that in the case of high moisture coals, following Brodie's method, it takes a much longer time (more than three hours) for the complete expulsion of moisture. Whereas using a pair of watch glasses of 2" diameter and taking one gram of coal, according to the method of the British Fuel Research Board, the moisture content was completely driven off in about an hour's time. It is well known that in the determination of moisture the loss in weight is actually the sum of two opposite factors, namely, one due to the evolution of moisture causing decrease in weight and the other due to prolonged heating causing an increase in weight by the incipient oxidation of coal particles without any evolution of gas Hence we find that in order to avoid slow oxidation the moisture determination should be finished in the shortest possible time

Now about the receptacle for coal it may be pointed out that the vessels should be properly and carefully selected and the author suggests that the recommendation of the British Fuel Research Board in this matter should be followed.[12] Suitable vessels recommended by the Board are as follows.—

(i) Glass petri dishes about 10 mm high
(ii) Shallow silica dish
(iii) Shallow stoppered weighing bottles
(iv) Watch glasses with ground edges held together with a clip Watch glasses with clip were also found to be the most effective drying vessel by W F Hillebrand.[13]

The Board points out that the weight of coal and the dimension of the dish should be arranged to give a layer of coal weighing not more than 0·3 gr. per sq. cm of exposed surface

A thin layer of coal on the watch glass will facilitate the almost complete evolution of moisture in about one hour's time It has been already shown by the author that in the narrow type of weighing bottle the moisture could only be expelled by prolonged heating for several hours. And in such procedure partial slow oxidation might ensue vitiating the result for real moisture value The author also points out that if the American method is followed, in the high moisture coals, the expulsion of moisture may not be complete in exactly one hour's time, but on the other hand some types of coal may require a little longer time The author therefore suggests that in the determination of moisture the American method should be a little modified as given below:—

About one gram of the air-dried sample of coal (60 mesh) should be taken in a pair of watch glasses, of about 2-inch diameter fitted with clip. Any other shallow vessel may be used but the recommendation of the British Fuel Research Board to which attention has already been drawn should always be borne in mind The watch glasses with the coal substance should be heated in a constant temperature oven for one hour at 105°C.–110°C. The pair of watch glasses is taken out of the oven and allowed to cool in a desiccator charged with conc. sulphuric acid and the first reading is thus obtained. Then every ten minutes the coal should be taken out of the oven, allowed to cool in the desiccator and weighed. The end point will be reached when a little increase in weight will be noticed showing conclusively that the slow oxidation has started in the coal substance. The previous reading should therefore be taken into account and calculation should be made accordingly.

It has been found in practice that it is generally difficult to get a constant weight in the course of an operation to find out the moisture and hence it is not easy to follow the suggestion of Brodie to determine the moisture by heating to a constant weight

About cooling the dried coal in the desiccator one word of explanation is necessary It is well known that powdered coal is capable of taking up a little moisture from the air but when perfectly dry or when dried at 105°C. it becomes highly hygroscopic and it has been experimentally found by the author that such dried coals, on exposure to air for even a short period, will show appreciable increase in weight Thus powdered coal (1 15 gram) exposed to air for two days was found to absorb 0 0017 gram of moisture while an equal weight of coal from the same specimen bottle when dried and exposed to air for one hour absorbed 0 0647 gram of moisture

It has been shown by the South African Committee[14] on coal, by N W Lord[15] and also by W F Hillebrand[16] that coal dust after complete drying is excessively hygroscopic, probably even more so than calcium chloride From the above consideration it is needless to point out that in the determination of moisture the desiccator should in all cases be charged with conc sulphuric acid and not with calcium chloride This point has been lost sight of in the method published by Brodie

In the process of weighing a little precaution is necessary to guard against the possible sources of error due to the reabsorption of moisture by the dried coals from the atmosphere, especially in the wet season Hence in the determination of moisture the specimen should be weighed as quickly as possible It should be mentioned in this connection that the 'inherent' moisture of coal should always be determined and the result given everywhere should indicate the percentage of the 'inherent moisture' only To get rid of the superficial water the sample as received should be crushed coarsely and allowed to remain exposed at room temperature for at least two days before being subjected to chemical analysis for the determination of 'inherent moisture'.

Now regarding the determination of volatile matter Brodie[17] has advocated two stages of heating The first stage of heating is done over a small bunsen flame for three minutes and in the later stage much stronger heating is applied for four minutes by subjecting the crucible to the hottest part of the burner $\frac{7}{16}''$ in internal diameter giving a flame 7" high; the crucible is then allowed to cool, the lid removed and the film of carbon adhering to the lid and a similar one on the side of the crucible are cautiously burnt off. The crucible is allowed to cool again in the desiccator and when cold it is weighed. It is quite clear that the procedure is not sufficiently definite from a scientific point of view.

We know that the volatile matter consists of gaseous and liquid products evolved from coal when it is subjected to destructive distillation and that coal is a mixture of substances possessed of different thermal stability. Volatile matter in coal therefore varies according to the temperature employed and it also depends on the degree of fineness of coal, nature of apparatus, time of heating and the amount of moisture. It is also known that the higher the temperature the greater will be the percentage of volatile matter Therefore the determination of volatile matter is a purely empirical procedure and concordant results can only be obtained by the adoption of a standard procedure by heating the coal at a standard temperature for a standard length of time The dimension of the platinum crucible, the length of the flame and the position of the platinum crucible with respect to the burner should also be standardised Brodie has given sufficient details regarding the dimension of the burner and the flame, but very unfortunately he is silent regarding the other points

If we refer to the standard methods adopted in different countries for the determination of the volatile matter we find that the temperature at which the coal is to be heated and the period of heating are practically the same In the American[18] and the British Fuel Research Board[19] method the heating is maintained at about 950°C for exactly 7 minutes If we are going to have concordant results of a comparable type in the determination of volatile matter it is better that we should either follow one of the standardised methods as outlined in the other countries or we should modify it to suit our own requirements But in the report regarding the method adopted in the Alipur Test House we find that the temperature factor has been totally neglected though the measurements of the burner and the flame have been accurately given A reference to the different standard methods will at once show that in the determination of volatile matter it is required from time to time to detect and check the temperature of the crucible by means of a thermocouple or by melting potassium chromate crystals in the crucible Recent researches of D F Smith and F A Hartgen[20] of the U S Bureau of Mines have shown that the melting point of potassium chromate (C P) is about 963°C A reference to the above work also shows that according to the older views the melting point of potassium chromate was found to vary within certain limits (between 940°C and 975°C). It has been pointed out in the standard methods[21] that specimens of coal having a high percentage of moisture or occluded gases should be heated gently for two minutes or so over a small bunsen flame, in order to avoid mechanical loss by rapid escape of steam and volatile matter, before the crucible is subjected to seven minutes' full heating at 950°C ±20°C. According to Brodie coal should be heated strongly for four minutes and not for seven minutes As the temperature factor has not been taken into consideration by Brodie and as the period of heating followed by him is also different from that generally adopted, it is quite clear that the result by Brodie's method will not be comparable with those obtained by following the standard methods. Brodie does not appear to have given sufficient reasons for such deviation from the standardised methods adopted in America, England, etc. Fluctuation in the pressure of gas supply, variation in the composition and quality of the gas, etc., may have some influence in maintaining uniform temperature.

From what has been said above it is quite clear that the standard flame of 7" high as recommended by Brodie may not always give in the laboratories situated in the different parts of India the desired and definite temperature of 950°C ±20°C, at which the coal is to be heated for the determination of volatile matter. The writer of this note actually found in the laboratory that with 7" flame of a bunsen burner having about ½" diameter, potassium chromate crystals could not be melted in a platinum crucible whereas with the same gas pressure the melting of potassium chromate crystals was effected by substituting the bunsen burner with the meker burner (No 3 or 5). That the use of the meker in place of the bunsen burner is more advantageous has been shown clearly by F. H Wagner[22] who writes

> 'The use of Meker burner is recommended by the Bureau of Mines in place of Bunsen burner owing to its superiority over the latter, especially for natural gas The construction of the Meker burner practically eliminates the fluctuating inner cone of the ordinary Bunsen flame, and thus produces a solid flame of fairly uniform temperature, this flame completely enveloping the bottom and sides of the crucible'

In order to overcome the fluctuating flame of the gas burner on account of excessive draught the British Fuel Research Board[23] has recommended the use of the Davies furnace, the utility of which was also pointed out by Cunningham Hughes[24] The author of this note also found this little apparatus of some use and suggests that in the case of fluctuating gas flame this type of furnace or some other kind of chimney as recommended by the U S. Bureau of Mines[25] may be used to secure a steady flame.

It is seen therefore that in order to maintain the definite temperature of 950°C.±20°C. for a definite period of seven minutes, sufficient precaution is necessary, but if an electrical furnace is available the above-mentioned difficulties can easily be overcome The U S. Bureau of Mines has recommended the use of such an electric furnace for the determination of volatile matter. In the Lessing method[26] also we find that coal is to be heated in silica tube in an electric furnace for seven minutes at a temperature of 950°C It is needless to point out that in the electric furnace we have got an absolute control over the temperature and there is no possibility of any fluctuating gas pressure or the loss of heat by radiation

From what has been stated above we may expect that the percentage of volatile matter obtained by following Brodie may be a little lower than the corresponding value of volatile matter obtained by following the standard methods either American or of the British Fuel Research Board A reference to the results obtained and given below shows that in the high moisture as well as in the low moisture coals the percentage of volatile matter after the American method was greater than that determined by Brodie's method.

%	High Moisture Coal (Burma)				Low Moisture Coal (Ekra, Jharia)			
	Namina		Kalewa		XI Seam		XIV Seam.	
	Volatiles	Ash	Volatiles	Ash	Volatiles	Ash	Volatiles	Ash
American method (modified)	39 60	3 70	42 30	3 00	19 92	18 82	20 10	12 80
Brodie's method	37 80	3 70	40 40	3 00	17 23	18 82	18 50	12 80

After the determination of volatile matter the coal was burnt to ash and from the figures in the above table we find that the ash percentage remains the same in both the cases showing conclusively that there was no loss of coal particles during the time of heating. We also find that according to Brodie[27] after driving off the volatile matter the lid of the crucible has to be taken out while the soot deposited on the bottom of the lid and inside the crucible is to be cautiously burnt off This procedure of heating the crucible with the lid open in presence of air is undesirable as somebody may carry on the heating operation for a comparatively longer period and in that case the coke may be partially oxidised In some high swelling coals the coke fills up the entire height of the crucible and sometimes touches the lid, thereby making it impossible to open the lid Hence we find that the method introduced by Brodie cannot be universally applied with all types of coal Moreover, it has been found that the lid contains a negligible amount of soot when the American method is followed whereas an appreciable quantity of it remains on the lid and the sides of the crucible when Brodie's method is applied, showing conclusively that the temperature was a little lower in the latter case than in the former.

From the above considerations we find that the method adopted in the Alipur Test House to determine the volatile matter is not up to the mark and differs in some respects from other standard methods Hence we are led to conclude that the procedure of Brodie should be modified before it can be regarded as a standard method for the estimation of volatile matter

Certain discrepancies in results due to non-adherence to any standard method have been observed in the Geological Survey of India laboratory. It was found by Dr. Fermor [*Rec. Geol Surv Ind*, Vol 62, pp. 192–194, 203 (1929)] that there was a difference of as much as 5 per cent in the volatile matter of the same coal obtained in the years 1919 and 1928 and this difference was ascribed to a change of the crucibles and the lower gas pressure in 1919 as compared with 1928. This shows that the temperature factor was not given due importance during the time of analysing coal in the Geological Survey laboratory.

The author of this note suggests the following procedure which is the American method with slight modifications:

Method ·

Apparatus · Meker burner (No 3 or 5).
Coal (60 mesh, I M M)
Platinum crucible with tight-fitting lid Capacity 30 to 40 c.c
Weight varying from 25 to 48 grams

The position of the crucible should be about 2 cm above the meker burner and the flame of the burner should be about 16 cm. enveloping the crucible so that no oxygen may have any access in the crucible About 1 gram of coal should be heated in the full flame of the meker burner for exactly seven minutes at about 950°C ±20°C If the flame becomes unsteady, the Davies furnace or any other device should be used to overcome the draughts In case of high moisture coals and cracking and salty coals and with those that decrepitate on heating due to large amounts of occluded gases, a preliminary gentle heating over a small flame for about two minutes (the period of heating depending on the nature of the coal) will be necessary This preliminary heating should be followed by full seven minutes' heating on the meker burner at 950°C ±20°C If in the case of some coals it is found that some fine coal particles are actually mechanically carried away on account of the sudden evolution of a large amount of hydrocarbons that are produced at lower temperature, then a preliminary gentle heating will be necessary to avoid such a disaster After heating for seven minutes the crucible is allowed to cool undisturbed in the desiccator charged with conc. sulphuric acid and then weighed. The loss in weight represents the volatile matter expelled plus the moisture in the coal. Then the percentage of volatile matter is calculated The dimension of the crucible and the weight should also be standardised within certain limits, as unusually a big and heavy crucible will take away much heat before the desired temperature is obtained, whereas a smaller crucible of much lower weight will be almost immediately heated to 950°C

About reporting the analytical results it has been the practice in some places to submit the analyses of coal on 'moisture-free' basis In the Alipur Test House the coal is dried to a constant weight at 105°C and then the dried coal is transferred from the weighing bottle to the platinum crucible and the volatile matter and the ash contents are determined from the dried sample. The moisture percentage is shown separately.[28] According to the standard methods [29] undried coals are analysed for the determination of volatile matter and ash.

The question whether the dried coal should be analysed has been discussed by the South African Coal Committee [30] and the U S. Steel Corporation[31] and they did not recommend the method of analysing dried coal but were of opinion that the air-dried sample should be analysed and, if necessary, the amounts of volatile matter and the fixed carbon might be calculated on the 'moisture-free' basis It has been shown by the present writer in the foregoing pages that it is difficult to get a constant weight of coal during the time of driving off moisture and it is quite possible that on account of the highly hygroscopic nature of the dried coal, there might be some error due to the absorption of moisture, vitiating the results for the real values of volatile matter and fixed carbon The author is therefore of opinion that the method of analysing 'air-dried' sample and not the 'dried' sample should be standardised and introduced everywhere and the results thus obtained may be recalculated to give the figures on 'moisture-free' basis.

Regarding the sulphur determination as adopted in the Alipur Test House, Brodie[32] has mentioned that the difference between the total sulphur in coal and the amount of sulphur present in the ash of the same coal is the amount of 'volatile sulphur' A reference to literature[33] available on the detailed sulphur study will at once show that the term introduced by Brodie is rather misleading The amount of sulphur expelled during the complete combustion of coal is known as the 'combustible sulphur' as distinct from the volatile sulphur which is the amount of sulphur that is driven off when the coal is carbonised at 950°C for the determination of volatile matter The 'combustible sulphur', however, includes the total amount of 'volatile sulphur'

Regarding the determination of ash, the residue left behind in the crucible after driving off the volatile matter should be heated in the flame in free access of air until all the carbon particles are completely burnt off with occasional stirring by a platinum wire The crucible may be heated with the lid open After complete combustion the ash may be carefully examined if any carbon particle has been left unburnt The end point will be reached by getting a constant weight

The value of fixed carbon is estimated by deducting the percentage of ash from that of coke

In conclusion the author wishes to draw the attention of the coal producers and coal consumers to the fact that the proper valuation of coal from the results of proximate analysis is only possible when such analyses are done by some standardised method, and he thinks that as there is no fixed method adopted by the coal analysts in India the time has come when one definite method for the proximate analysis of coal should be standardised and adopted everywhere The author also draws the attention of the National Institute of Sciences of India to this important problem

The author has made an attempt to outline in the foregoing pages one such method for the estimation of moisture and volatile matter He also suggests that so long as there is no standardised method it is really necessary that every proximate analysis of coal published should be accompanied with a definite statement regarding the method adopted so that one may have a proper idea about the accuracy of the result

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METHODS OF ANALYSIS OF COAL IN INDIA

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There is probably no subject so pregnant with possibilities of dissension and acrimonious dispute than this hardy annual of methods of analysis of coal. The reason is obvious We still, after several decades of intensive research on coal, do not know much about it And when trying to analyse a substance whose chemical composition is still a mystery it is obvious that we cannot yet with confidence say that such and such a chemical procedure will give precisely such and such information about the substance We have, therefore, to fall back upon agreed-upon methods of investigation and, further, we have to impose upon ourselves this and that restriction as to conditions of each experimental test, otherwise discrepant results obtained by different workers would merely be perpetual sources of disagreement and misunderstanding

The rest of the technical and scientific world has long since agreed upon the necessity for adopting this attitude. India alone, it would appear, has not yet fallen into line and at this important stage in the development of industry in India, and especially at this stage in the history of mining and utilisation of coal in India, it is particularly unfortunate that it should still be necessary to reiterate the warning given by the author and others during the past ten years. Scientific research is progressing by leaps and bounds in this country and Fuel and Safety in Mines Research is at last coming into its own The tragedy of the position is that for want of agreement upon this most vital and fundamental matter, the adoption of and adherence to standard methods of analysis of coal, probably more than 90 per cent of the work done on coal in this country during the past decade is of little scientific value Years of otherwise valuable research work have been spent unprofitably and most of the investigational work that has been done will have to be repeated.

This is a subject that many have written on in recent years. Probably the most important authentic recent reference in the literature in India is the paper by Brodie in the *Records of the Geological Survey of India* (*Rec* LXIII, 1930, Part 2, 189) with the accompanying note by Fermor. Its importance lies not in the value of the methods outlined but in the fact that the methods described are not those approved by the scientific and technical world. The laboratory in which the methods referred to by Brodie is that in which are analysed the coals of our two most important coalfields and it is on the results of these analyses that coals are graded in India. Further, it is largely on the grading thus achieved that the prosperity of the coal industry depends. As no authoritative statement appears to have been issued to the contrary it is assumed that these methods are still in use and the consequences appear to

VOL. VI—No. 3. [Published August 22nd, 1940.

the author sufficiently important, both from the scientific standpoint and from the point of view of the industry, to justify examination.

It is probably hardly necessary to state that analyses of coal are of two kinds, ultimate analyses furnishing information regarding the percentages of elements such as carbon, hydrogen, oxygen, sulphur, etc., in any coal and so-called 'proximate' analyses, indicating the proportions of what, for want of a better concise term, we may perhaps call the different components of a coal, the moisture, carbonaceous volatile matter, 'fixed carbon' and ash. In this *Symposium* it is assumed that all taking part are quite familiar with the meanings and full significance of those terms We here are concerned with aspects of the matter that particularly affect us in India, with such questions as 'What differences are there between the methods used by various investigators?' and 'What justification, if any, is there for departing from what is generally adopted elsewhere throughout the world?'

It is sufficient if we examine the methods at present accepted as standard and certain known examples of departures from those methods

Fortunately the scope of our enquiry can be limited. So little work has so far been done on ultimate analysis of coal that even if it had not been done according to accepted methods little harm would have resulted But the methods that are suited for carrying out ultimate analyses are in any case standard, or more or less standard, methods of chemical analysis throughout the world There is little risk, therefore, of the results of such ultimate analysis as have been done being inaccurate on account of the methods employed

It is when we come to proximate analysis that we encounter a different state of affairs. And it is one the importance of which it is extremely difficult to impress upon anyone who has not himself performed such operations as are involved, still less anyone who is not himself a fuel technologist or even a scientifically trained person The various 'components' are dealt with below, after reference to Preparation of Sample.

PREPARATION OF SAMPLE.

Perhaps a preliminary reference to Collection of Sample should be incorporated here It is remarkable how this fundamental preliminary is improperly attended to and what extraordinarily stupid mistakes can be made when submitting samples for analysis. It is still no unusual experience for the author to be presented in his laboratory with a single large lump of coal with the request to have it analysed for the purpose of judging the quality of a seam of coal. It is needless to point out that in such a case it is almost unquestionably a waste of time even to carry out the analysis. The mining public and buyers and sellers of coal still require a certain degree of education in this matter. It must be admitted, of course, that extremely stringent conditions regarding the taking of a perfectly representative sample need not always be observed. There is such a thing as exercising discretion.

An important preliminary to preparation for the actual analysis is the removal of surplus moisture The Fuel Research Board and most other official authorities specify that the sample weighed out for analysis shall be air-dried Now air-drying is admittedly an uncertain procedure, especially in a tropical climate, and yet it is conceivable that we can agree upon a method to suit India Drying inside a laboratory for 24 hours by laying the large sample out in a layer on a bench would appear generally to be suitable, except during the wettest period of the monsoon. During the cold weather and the hot season the author finds it sufficient to lay the large sample out on a verandah (on a sheet of clean paper), gently stirring it about from time to time especially if it is visibly wet Obviously the amount of moisture still adhering will depend to a certain extent upon the degree of humidity and the atmospheric temperature on the day on which the sample is dried. This would appear to be a useful line of research for a beginner in this work.

Apart from selecting a method for preliminary drying it is important also to note that the amount of loosely-held moisture thus lost may have to be determined. Agreement between the coal supplier and the analyst is essential in this matter.

The method adopted by the United States Steel Corporation for air-drying of visibly wet samples might well be adopted for Indian conditions It consists of passing over the sample a continuous stream of air, at a temperature of 10° to 15° Centigrade above room temperature, until the sample is of approximately constant weight. But it also applies a maximum temperature of 35°C. (95°F.) which would not always suit Indian conditions Perhaps it may prove necessary to discontinue attempting in India to do accurate scientific fuel analysis in certain seasons.

Apart from the matter of air-drying we come to powdering the gross sample. The Fuel Research Board specifies 60-mesh powdered coal. This is practically universally prescribed and should be adopted in India. The crushing and sifting, of course, should be done as expeditiously as possible to avoid continual loss of moisture in the process.

MOISTURE.

Here again we come to a determination on which it is absolutely essential that we agree. The standard method prescribed consists in heating one gramme of the 60-mesh air-dried coal for one hour in an air oven at a temperature of between 105°C. and 110°C. Now mere heating in an air oven at the prescribed temperature is not sufficient. The air in the air oven must be changed several times during the heating In well-equipped laboratories specially designed air ovens are available for this purpose. Where such luxuries are not available the author suggests gently opening the door of the air oven till it is as wide open as possible and then closing it again, choosing a time when the temperature has risen to 110° or nearly so. Experience shows that consistent results can thus be attained without any further elaboration of apparatus. When the author is carrying out a large series of analyses at a time he relies upon the simple expedient of opening the oven door at approximately 10-minute intervals, using a laboratory alarm clock when available. When the laboratory alarm is in use for other purposes he times the opening of the oven door by the time taken for determining volatile matter in other samples. By this means, maintaining a temperature of about 110°C. in the oven, the moisture-laden air at that temperature is periodically swept out and replaced by fresh, comparatively dry air which soon attains the temperature of about 105°.

In determining moisture it must be remembered that the layer of coal should be evenly spread over the dish. The Fuel Research Board specifies a layer not more than 0·3 gm per square centimetre of exposed surface. The Government Test House method described in the paper referred to above allows for taking 'about 2 gm in a weighing bottle' Presumably a fairly thick layer of coal results and it would appear as if the moisture-laden layer of air immediately above the heated coal does not have a reasonable opportunity of escaping, and the remaining moisture in the coal underneath is not likely to be fully driven off.

This is a matter of great importance in India as the grading of coals depends to a large extent upon the amount of moisture thus determined In this respect the Government Test House (if it still adheres to the methods described by Brodie in the paper referred to) differs from practically all other experimenters and in consequence the grading of coals in India by the Indian Coal Grading Board cannot, in the case of high-moisture coals, be that calculated by any experimenter using standard methods.

This is a matter on which agreement should be aimed at.

VOLATILE MATTER

In determining the amount of volatile matter other than moisture, the standard method prescribed a platinum crucible with tight-fitting lid, the crucible of particular dimensions, the using of exactly one gramme of 60-mesh air-dried coal and heating for 7 minutes to 925°±25°C. Platinum crucibles are expensive and many analysts may have to be content with porcelain crucibles and Bunsen burners It is true that results of value to the industry for most practical purposes may be obtained by the cruder method. The standard method does not specify the use of an electric furnace, but points out that where an electric furnace is available porcelain or silica crucibles may be used. For accurate work, for grading and for all research work the platinum crucible must be used if no electric furnace is available, and there must be some accurate method of ascertaining that the correct temperature range has been attained.

The author uses at present an electric muffle furnace always maintained at about 950°C. The frequent opening of the door causes the temperature to fall and in practice the range 925°±25°C. is attained with little difficulty. Ash determinations are not carried out in this furnace. Where an electric furnace is not available some sort of shield is necessary to ensure that the sides and top of the crucible are more or less uniformly heated If one of the approved Davies type cannot be made up, a useful expedient is to surround the crucible, when it is on the pipeclay triangle, with teased-out stringy asbestos This acts as an excellent radiator of the heat of the burner flame and a light layer of the same material on the lid completes the furnace effect

Some experiments prescribe removing the lid of the crucible and burning off the 'coke' layer formed thereon That should not be done There are other precautions to be observed, but it will probably be agreed that they are not materially affected more by Indian conditions than by those in other countries and, accordingly, they are not discussed here

FIXED CARBON

As this 'component' is determined arithmetically it will not be discussed here

ASH

Owing to the important chemical changes that may take place in the mineral matter present in a coal in the course of burning it, the temperature to which it is heated may greatly affect the weight of residue obtained In order to minimise discrepancies due to this cause the standard method prescribes a temperature of from 750° to 800°C The sample is heated for one hour (or till constant in weight) in an oxidising atmosphere The author uses a muffle furnace kept at a temperature of about 780°C The Government Test House method described in the paper referred to above prescribes a temperature of 1000°C The Test House method referred to also uses, for this determination, the coke obtained from the volatile matter determination Although coke is usually rather more difficult to burn to ash than coal the use of the coke obviates the difficulty that arises in the case of coals liable to mechanical loss through the coal splitting up on initial heating If the extra time required for using the coke can be spared, therefore, the procedure is a useful one The temperature prescribed, however, is much too high and is liable to give inaccurate results in those instances where kaolin, gypsum, some carbonates, common salt, etc (liable to decomposition or volatilisation at the higher temperature) are present Whether there is much risk of error from this cause in Indian coals is not known at present This would be an interesting and important line of research.

DETERMINATION OF CALORIFIC VALUE.

Almost the only important statement to make in this connection is that no calorific value that has been determined otherwise than in a first-class bomb calorimeter should be given serious attention Other methods of ascertaining approximate calorific values have their uses. The author himself has devised a formula for calculating calorific value from the data of the proximate analysis and it has proved extremely useful as a check But such calculation methods should not take the place of the use of the bomb, and other cruder apparatus such as the Lewis-Thomson calorimeter are only of use for purposes of rough comparison

METHOD OF REPORTING ANALYSES

There are several ways in which the results of a Proximate Analysis can be recorded For example the amount of loosely-held moisture lost during air-drying may have to be recorded and that should be kept in mind prior to preparing the sample for the laboratory Then the amount of moisture found by drying the 60-mesh air-dried coal in the air oven at between 105°C and 110°C may be shown in the total analysis, or a separate analytical statement regarding the moisture-free coal may be given, but in the latter event there must be some manner of showing what amount of moisture was present. Normally it is better to give a double or triple statement showing the analysis of the coal (*a*) as received, (*b*) as 'air-dried sample', and (*c*) moisture-free

Then it is frequently desirable to indicate the composition of the 'pure coal', *i e* the combustible substance originally present in the coal. A statement of analysis on such a basis is described as being given 'on the dry, ash-free basis' The above are the most usual types of statement used or asked for We have in India yet another type of statement, the one used officially by the Indian Coal Grading Board In effect it is to some extent a compromise between the standard 'air-dried' sample method of recording and an 'oven-dried' sample method In the single statement recording the results of the analysis the amount of moisture is shown (as determined in the air oven) and then the remaining items of the orthodox proximate analysis are shown, but they (without the moisture at the head of the statement) total 100 Including the moisture shown in the analysis the total, of course, would come to more than 100.

The calorific value is, in the standard method, shown for the coal according to the method of recording the results of the proximate analysis For example if the coal has been air-dried the calorific value of the air-dried coal is shown If a separate statement of the proximate analysis of the moisture-free coal or the 'dry, ash-free' coal is given then the calorific value as actually determined is re-calculated on the same basis and shown in the adjusted statement.

The reason for referring in such detail to this matter is that on account of the lack of agreement in India as to the method to be adopted to show the results of proximate analyses there are serious discrepancies in interpreting them.

Fortunately the discrepancy is not a serious one in the cases of the majority of Jharia Barakar coals, whose moisture content is seldom more than one per cent (though the error referred to below exists even in those cases). But in the case of high volatile coals there cannot but be reasons for misconception when critically examining the statements of analysis recorded by the Coal

Grading Board method, and those of us who are concerned in the winning, preparation and utilisation of coal in India should be fully alive to the possibilities of error

A high-volatile coal, for example, usually, in India, contains a high percentage of moisture that would be driven off in the air-oven A high-moisture high volatile Raniganj coal, containing about 7% of moisture, may be taken for the purpose of illustration The statement of analysis of such a coal according to the several possible methods is given below and will repay close examination

There are two important effects that operate in opposite directions, when judging the value of a coal by examining the analysis as reported according to standard methods and according to our official practice in India The first is that the Indian official practice shows a high-volatile coal as having a higher calorific value than it really has, in the example given the calorific value being recorded as 6,458 calories per gramme, whereas the calorific value of the coal 'as received' is only 5,841 calories and that of the air-dried coal only 6,000

On the other hand, the same coal is shown by the official Indian method as having 14 60 per cent of ash whereas the coal as received has only 13 21 per cent of ash and the air-dried coal only 13 52

In other words the official Indian method of reporting coal analyses accords to high-volatile moist coals a relatively better calorific value and a relatively higher ash content than it does to low-volatile coals If the one effect cancelled or 'neutralised' the other no great harm would result, but that does not happen

Apart from the unrealised possibility of these two effects tending to neutralise each other it is more important to note that the official Indian Statement or Report of Analysis does not readily indicate to the purchaser what he is buying.

STATEMENT OF ANALYSIS OF A HIGH-VOLATILE INDIAN COAL ACCORDING TO DIFFERENT METHODS OF REPORTING

Statements according to internationally-accepted standard methods compared with C G B. *method*

	Coal as received.	Air-dried coal.	Calculated to dry-ash-free basis	Coal Grading Board method.
Moisture	9 55	7 40		7 40
Volatile matter less moisture	28 49	29 19	36 92	31 50
'Fixed carbon'	48 75	49 89	63 18	53·90
Ash	13 21	13 52	.	14 60
Colour of ash .	Light reddish brown.			
Character of coke	Moderately coherent.			
Calorific value. (Calories over gramme) .	5,841	6,000	7,060	6,458

It will probably be agreed by all fuel technologists, and it ought to be agreed by all sellers and purchasers of coal in India, that this anomalous position should be rectified

Unfortunately, closely bound up with this matter of adopting standard methods of analysis and of reporting the results is the whole commercial system on which has been built up in recent years the stability of the Indian coal trade There is naturally a fear, among mining interests, that any 'tampering' with the present system of grading of coals would endanger the trade The author does not agree In order to rectify the matter it would not be necessary either to abandon the present system (in general) of grading coals nor would a coal at present in any particular grade be placed in another grade All that would be necessary would be to adhere to the existing grading and, in re-wording the specification according to which the grading is at present carried out, the arithmetical changes necessary would be calculated and applied to grading of coals submitted for grading in the future Except in so far as a very few particular coals might be found to be graded too low or too high according to the present method of reporting, no material change would take place And purchasers would be better able to compare one coal with another, which they cannot satisfactorily do at present

Other Determinations

It is not considered necessary to refer in detail to the other components, such as sulphur and phosphorus, as are sometimes determined, as no particular difficulty arises that is peculiar to India But reference may with advantage be made to one test the importance of which is growing, namely, the determination of the fusibility of coal ash Comparatively few coal ash fusibilities have been determined so far and fuel technology laboratories that are to be fitted up in future in this country should be capable of making this determination The author has a small amount of information on this subject, mostly of a confidential nature, but hopes shortly to be able to publish an authoritative statement regarding a large series of Indian coals Pending the liberation of that information it is sufficient to indicate some temperatures likely to be recorded

A selection of Raniganj coal ashes was found to soften at from 1140°C to 1290°C, their fusion points being shown to be from 1250°C to 1420°C The corresponding figures for a small selection of Jharia coal ashes were 1200°C. (for softening point) and 1230°C. to 1255°C (for fusion point) A mixture of Jharia coal ashes gave a softening point of 1100°C. and a fusion point (complete fluidity) of 1250°C These determinations were made in a normal oxidising atmosphere. [Note Later information gives a much wider range for coal of both those fields]

It will be noted that, as might be expected, the mixture of Jharia coal ashes began to soften well below the softening point of individual samples from the same field.

There is probably only one other point that calls for special comment and that is the determination of oxygen as well as of 'fixed carbon' The amount of oxygen in coal is usually determined by calculation, after taking into account the distribution of the various other elements and radicles known to be present in the coal, and the amount of fixed carbon is determined arithmetically 'by difference' But it is impossible to say in what form the incombustible mineral matter that gives rise to the ash exists in the coal and it is definitely known that the amount of the ash may be, and usually is, less than the amount of mineral matter that produced it An average of seven-eighths is frequently assumed, but the matter is an extremely complicated one and much research work, especially by the well-known American worker Parr, has been devoted to this subject. The average figure referred to means that a coal shown to have 14% of ash may really contain 16% of useless mineral matter In consequence the figure shown in the Report of Analysis for Fixed Carbon is too high and, in consequence, the classification of the coal by the usual methods is incorrect For similar reasons the determination of the amount of oxygen in Indian coals cannot yet be accurately carried out. This is an important field for the research worker

COAL CLEANING AND BENEFICIATION IN INDIA.

By C Forrester, *A H W C*, *F I C*, *Ph D*, *F R S E*,
Fellow of the Institute of Fuel

The subject of cleaning of coal is, in India, one that has probably received a greater amount of discouragement than any other affecting the winning and utilisation of coal Comparatively little has been done in the matter of either research work or practical experiments As far as Indian conditions are concerned, therefore, there is unfortunately little that can with confidence be said on this subject and what little is known mainly concerns Jharia and Raniganj coals In this connection Mr Innes' remarks in his paper (this *Symposium*) on the marketing of coal in India are worth special attention

The beneficiation of coal may be effected in several different manners, for example by hand-picking underground or (more usually) on the surface, by carefully planned screening, by 'washing', *i e* by removal of heavy (and therefore high-ash) material by treatment in currents of water or by liquids of selected specific gravities, by 'dry cleaning', utilising various physical properties of coal and shale or stone such as coefficient of friction, elasticity, resilience, etc, and so on All these processes are based on the assumption that stony material occurring along with coal is to a large extent separated from the better quality coal in the ordinary processes of mining and the subsequent normal preparation of the coal for the market

Most practical mining men in India assert that the bulk of the ash-forming mineral matter in Indian coals is much more intimately mixed with the coal substance than is the case in countries (*e g* Britain) where coal cleaning is extensively employed To a large extent that is true and it must be accepted as an unfortunate fact that coal cleaning methods are much less likely to meet with success and universal adoption in this country than in most other countries But other countries possessing coals very similar to those found in India have taken up this matter seriously and the mining industry of India will be committing a grave mistake having effects lasting for many generations if it does not maintain interest in this subject

As with so many other problems that interest the scientist there are serious economic aspects of this question We have not yet, however, reached the stage at which the economics of the matter can be profitably pursued and it is not at present proposed to deal with them. For the purposes of this note, therefore, we shall deal with the scientific aspects and such practical aspects other than economic that the information available justifies referring to.

There is already in operation in India a kind of coal cleaning imposed, in a sense, on the industry but it is the most expensive and least efficient coal cleaning in the world. The conditions in which the Indian Coal Grading

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Board issue Grading Certificates are such that all colliery concerns that desire to obtain, and retain, such certificates must exercise a wholesale selection of the better portions of seams and also a considerable amount of hand-picking both underground and on the surface It only requires a few visits to selected collieries in both the Raniganj and Jharia coalfields to realise the extent to which shale and stony coal *do* exist in a separable form The author is inclined to wonder whether the coal mining industry realises the full significance of this fact when considering coal cleaning But there is a more important aspect of this that deserves greater attention that it receives It is an inevitable consequence of the Coal Grading Board method of grading coal that, in order to retain a certificate, certain lower grade portions of seams are left underground A small fraction of one per cent in ash or calorific value may frequently decide in favour of or against a considerable proportion of our coal reserves and the slow adoption of the principles of buying and selling according to specification, allowing for penalties *and premia* for departure from the specification, cannot but militate against the adoption of proper cleaning processes

The present author has not collected data regarding the results of hand-picking and his figures relating to portions of seams left unmined on account of the practical and economic difficulties at present in the way of the adoption of modern methods are insufficient to justify quotation This reference may, therefore, be taken as an invitation to practical mining men to give the rest of the industry, and scientific friends of the industry, fuller information that may aid in furthering the cause of coal cleaning and thus serve the industry as a whole

So far as regards the more commonly used methods of cleaning, particularly 'washing', little or nothing has been done in India, or if it has been done the literature does not help us much One firm has in recent years carried out practical experiments in dry cleaning, using the Berrisford separator, with encouraging results But dry cleaning processes are not generally likely to be so suitable for Indian coals as wet processes The differences between 'coal' and 'dirt' or 'stone' are not so clearly defined The gradations between the various qualities of coal are too gentle and it is in the opinion of the author doubtful whether dry cleaning methods are ever likely to be favoured

One special method of cleaning of coals utilises the principles employed in the froth flotation of ores and this process has also been tried, though only in the laboratory, for the treatment of Indian coals The work is reported on in the *Records of the Geological Survey of India* (Vol. LVI) and was carried out as long ago as 1924 by W. Randall. Compared with more recent investigations this report cannot now be regarded as affording us much reliable information about the cleaning of Indian coals. Modern methods of investigating the possibilities of cleaning coals require the construction of washability curves Much useful work on this subject awaits the investigator and it is not unduly difficult to do.

Perhaps the only published results of such investigations are those of the author, appearing as part of a paper on the Barakar Coals of the Jharia Coalfield (*Trans Min Geol Inst Ind.*, XXX, 1936) The work therein recorded relates to Jharia coals only, though a similar investigation (the results of which have not yet been published) had then been carried out on a selection of Raniganj coals

Along with this work on washability the author also examined the same series of coals by X-rays with a view to indicate the manner of occurrence of the high-ash material in the coals The results of these two lines of investigation can appropriately be referred to together Considerations of space in publication and time at our disposal in this *Symposium* make it desirable to summarise conclusions rather than to develop arguments

Apart from wide stone bands and other easily recognisable high ash bands in seams, high-ash portions of Barakar coals cannot be readily removed from large size or so-called 'steam' coal In this respect, of course, Indian coals do not differ very seriously from the best British coals Most profitable washing processes do not apply to large size coal It is when we come to examine the possibilities in respect of the smaller sizes of our coals that the difference is striking—and no doubt discouraging Large rubble coal obtained in the ordinary course of mining in say Britain may, and frequently does, contain innumerable pieces of stone and/or high-ash material This can be easily separated by almost any simple washing plant The same cannot be said, in general, about Indian coals, or, rather, it cannot be said about rubble of the same size, and it will probably have to be admitted that it cannot at present be said about any coal above say 2-inch in size, always excepting, of course, wide stone bands, etc , already referred to The abandonment of the present grading system would in all probability completely alter every aspect of this question

It is when we come to the smaller sizes of screened coal that the possibilities of cleaning on a large scale become more attractive Again excepting the wide stone bands,etc ,at present deliberately left *in situ* or hand-picked underground, we find that even the carefully selected coal can to some extent yield up varying proportions of high-ash material The washability curves of 23 Jharia coals appearing in the paper referred to above indicate that the smaller sizes of our Indian coals might respond to normal washing processes In considering the practical implications of these curves it must be kept in mind that they record the result of investigating crushed *clean* run-of-mine coal already selected for despatch as comparatively good coal If the methods of winning were such as to include a greater proportion of stony bands and high-ash coal, for separation on the surface, the slack coal would in all cases have shown a remarkably higher degree of beneficiation. Here is another direction in which much useful experimental investigation awaits the research worker The results of such work would go far to change the whole attitude of the mining industry to the subject of washing.

There is a subsidiary aspect of washing of coals in India that has not received the attention that its importance—its *practical* importance—merits. It is an aspect that only the iron and steel manufacturer fully appreciates There is no surer source of inefficiency and waste in blast furnace operation and foundry work, and probably to a less extent in steel manufacture, than a supply of coke of *widely varying* ash content Alternatively stated, it pays the blast furnace manager to work with a comparatively high-ash coke whose ash content, and the chemical nature of whose ash, do not *vary* appreciably over very long periods, rather than to work with a large series of cokes of different quality the ash contents of which are all comparatively low but vary within several points per cent as well as chemically

The practical results achieved in the laboratory by the author were, as already suggested, not all encouraging As much as 25 per cent to 30 per cent of the crushed or slack coal had to be rejected to lower the original ash content by one-quarter of its value But there were cases where as little as 5 per cent rejection effected the same beneficiation Remembering again that these tests were carried out on comparatively clean crushed coal the conclusion that appears to be justified is that washing of slack coal obtained by mining the whole of a seam (without rejection of coal of intermediate quality in order to 'get into the grade') would undoubtedly give excellent results, and of course add to the total output

Another result of such lowering of ash content, quite apart from the *amount* by which it is lowered, is that even a small reduction in ash content may be accompanied by (in fact, due to) the removal of highly injurious constituents of the ash, especially sulphur compounds as these occur in the *heavier* fractions removed in washing

Yet another practical aspect of this subject is concerned with screening and the accumulation of vitrain in smalls It is now well recognised that some Barakar seams, especially, in the opinion of the author, those in the Jharia coalfield, contain unusually friable vitrain In the ordinary course of mining, this vitrain naturally becomes liberated to a degree corresponding to the extent to which the coal is ultimately broken up for despatch. The greater the amount of rubble produced the greater the amount of vitrain that is likely to be liberated Vitrain has always a much lower ash content than any other portion of coal, the author's experiments give ash contents as low as 2 5% for vitrain of specific gravity below 1·3 (One sample from No. 14 Seam in the Jharia field gave the unusually low figure of 1·525% for ash) It is obvious that an accumulation of such low-ash material will have a beneficial effect on the slack coal among which it accumulates. The lower ash content of slack coal as compared with the steam coal from which it is derived and with the rubble (which has consequently, of course, a *higher* ash content than the steam coal) is a well known fact. But there is another interesting fact that merits attention. This enrichment of small coal does not proceed indefinitely. If a careful screening test is carried out on run-of-mine coal, especially coal that has been machine-mined, cutting having partly taken place in an undulating stony floor, the very finest material, *i.e* dust finer than say 90-mesh, may have an exceedingly *high* ash content, *e g* 60–65% Such high-ash dust can be removed by pneumatic methods, *e g* by allowing the fine coal to fall down a series of inclined shelves, between which a current of air is blown or sucked by an exhaust fan The whole operation is carried out in a suitably designed tower and the air rising to the top carries with it the high-ash dust The process is well known as 'de-dusting' De-dusting of coking slack may yet prove in this country to be a useful adjunct to the other coal washing operations, and is in fact likely to be adopted more particularly in connection with the cleaning of coking slack, not only to reduce ash but also to aid in draining of the washed product and to avoid slurry problems

In opening discussion on this kind of subject it is presumably not desirable to attempt to indicate what different kinds of industrial plant are likely to be adopted in India should coal washing become a common practice But the preliminary study that has so far been possible suggests the likelihood of the Reolaveur type of washery being particularly suitable for the treatment of coking slack in this country The author favours investigations by the coking and iron and steel industries into the possibilities of installing two or three collecting centres for washing slack by a plant of that type prior to shipment to the coke plants Alternatively one of the more recent specific gravity processes (e g chance) offer definite attractions, as they can be applied to unscreened coal

In conclusion of this brief summary of the position it may be suggested that much useful practical work can be done on Indian coals to provide the industry with statistics and the results of laboratory investigations, and especially work on run-of-mine coal from the whole of a workable seam, as well as on the slack from the same seam Fuller detailed information is required on this most important and essentially practical problem

COAL CLEANING AND BENEFICIATION

By E R GEE, *M A* (*Cantab*), *F G S*, *Geological Survey of India*

It is now recognised that at least a large majority of the coals of India are difficult to clean by any known wet or dry process This is due to the very fine state of division of much of the mineral matter and to its very intimate association with the coal substance

One might well enquire the reason for this unfortunate characteristic of most Indian coals as compared with many coals in Europe and America

The writer suggests that it is due to the fact that the coal seams of India—at least the Gondwana seams—are of drift formation in contrast to an *in situ* origin There is definite geological evidence in favour of the formation of the Gondwana seams from vegetable debris that has been carried down by rivers into low-lying tracts presenting conditions suitable for its accumulation During the course of transit, finely divided mineral matter would undoubtedly become associated with the organic debris and would also tend to impregnate the latter when it held partially decomposed into a soft gelatinous mass As a result, this mineral matter would become intimately associated with the coal substance

But, in pronouncing judgment on the possibility of cleaning the coals of India, one must remember that washability is a relative factor and the limiting economic conditions of one country or even of one particular area may be quite different from those of another

Thus, although it will probably be economically impossible to clean Indian coal so as to yield a product containing less than 12 per cent of ash, it does appear likely that the washing of inferior grades—particularly the Barakar seams of coking property—from an ash percentage of 20 to 25 down to some 12 to 15 This possibility has recently been referred to by Mr A Farquhar in his Presidential Address to the Mining, Geological and Metallurgical Institute of India Fine grinding, prior to washing, will doubtless be necessary and this will obviously enhance the cost appreciably.

On account of the intimate nature of the ash, an appreciable proportion of coal substance will doubtless remain along with the 'refuse' (the 'sinks') and the amounts of 'refuse' will no doubt be relatively large. Much of it will contain a percentage of ash as low as some 25 to 35 per cent. In view of the fact that pulverised coal containing up to 40 per cent ash can now-a-days be burnt successfully in furnaces fitted with suitable burners, it may well be possible to utilise much of the pulverised 'sinks' for steam-raising Obviously, it would not pay to transport this high-ash fuel to any great distance but, in conjunction with any large industrial schemes in the coalfields, such as

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the electric generating plants suggested in this Symposium, the use of this cheap fuel might deserve consideration

As mentioned previously in my note on the 'storage of coal', in any large enterprise involving pulverisation, the question of spontaneous combustion will have to be considered, though the liability to spontaneous ignition will no doubt be much less in the case of the high-ash products than with the relatively low ash coal

The subject is one on which considerable research is necessary both in the laboratory and on a larger scale, the possibilities of success are, I consider, not unpromising

SULPHUR IN COAL

By N N CHATTERJEE *

The presence of sulphur in the Tertiary coals of India attracted the notice of early workers[1] and in the analytical results published only total sulphur was recorded Moreover as granules and lumps of pyrite were easily detected in the hand specimens the sulphur content of the coal was attributed chiefly to pyrite by almost all the workers in India It has long been known that the high grade coals of Upper Assam on account of large sulphur content could not be efficiently utilised for many important uses Richard Smith,[2] however, in discussing the analytical results of Makum coals suggested that sulphur might be present in the coal partly in organic constituents and partly as iron pyrite and probably as sulphates But in the analyses published he recorded the amounts of total sulphur only

Though the presence of sulphur was noted by early workers and the railway authorities in Assam the knowledge regarding the sulphur compounds in the Tertiary coals of India was very meagre and no detailed work in this line was published It will be pointed out in a succeeding chapter that the total sulphur is not the only factor to be considered, but the amounts of different sulphur forms should be determined before any coal is recommended for particular use.

It may be mentioned in this connection that on account of the researches of Powell and Parr[3] our knowledge regarding sulphur in coal has recently been greatly widened As a result of investigations it has been found that sulphur in coal generally occurs in four different forms, namely (i) Pyritic sulphur; (ii) Sulphate sulphur, (iii) Organic sulphur, and (iv) Free sulphur.

The present author had an opportunity of studying a number of high sulphur Tertiary coals of India and he is highly indebted to Dr Fox for extending facilities for this work and also for his valuable suggestions.

It will not be out of place here to mention something regarding the source and origin of sulphur compounds in coal It may be pointed out that the coals formed under fresh water conditions have always a very low total sulphur content, whereas the coals formed under marine and brackish water or estuarine conditions have always a very high percentage of sulphur. This question has been discussed by several earlier workers who think that both pyrites and organic sulphur compounds are better developed under estuarine and marine water by biochemical processes helped by sulphur secreting bacteria (see Clarke—Data of Geo-chemistry, pp 150, 518) A certain amount of sulphate and pyrites is also formed by pure chemical processes.

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The sulphur compounds in coal might have been derived from various sources and in different ways as summarised below —

(i) Organic sulphur compounds originally present in the plants that are ultimately converted into coal Small amounts of organic sulphur compounds (proteins, etc) from vegetable debris are gradually concentrated in the final coal substance, as we know that about 10 ft of plant debris get compacted and reduced to make only one foot of coal seam

(ii) The soil on which the plants grew might have been rich in sulphur salts and sulphur secreting bacteria and the plants might have thus obtained a sufficient supply of sulphur compounds and, after assimilation, these salts were probably retained as various organic sulphur compounds, besides some inorganic sulphur salts Such plants might have better contributed to the sulphur content of some high sulphur coals The remains of sulphur bacteria might have given rise to sulphates in the soil to be ultimately used as plant food

(iii) After deposition in the marine and estuarine waters the vegetable debris were subjected to complicated process of putrefaction and coalification when complex chemical and biochemical changes started, together with the activity of micro-organisms under favourable conditions, as a result of which various sulphur compounds have possibly been formed and retained by the coals as their constituents In this way pyrites as well as many organic sulphur compounds have been formed by bacterial activity Some pyrites and sulphates might have also been formed by purely inorganic processes

Only unaltered and fresh specimens and those clean pieces having no pyrite patches were subjected to laboratory investigations During analytical work the methods adopted by Powell and Parr were generally followed In the fresh and unaltered specimens of Tertiary coals of India the author had been able to detect all the forms of sulphur except the free-sulphur While visiting some coalfields in the Khasi Hills (Assam) and Bokaro coalfield (Hazaribagh) the writer could however find in the weathered coal faces traces of free sulphur But this appears to have been formed by secondary changes during the process of weathering. Such altered and weathered specimens were not used for the quantitative determination of various sulphur forms

For pyritic sulphur determination 1 gm. of coal (100 mesh) is digested with 80 c c dilute nitric acid (1 3) and the solution allowed to stand at room temperature for about 4 days during which time all the pyrite will be completely oxidised and dissolved Any sulphate if present will also go into solution. The solution is then filtered, the nitric acid driven off by evaporation and the residue taken up in some water and hydrochloric acid The sulphur is then precipitated as $BaSO_4$ by barium chloride solution and the amount of sulphur in coal is obtained by calculation The value for pyritic sulphur is then obtained by subtracting the amount of sulphate sulphur determined separately

The sulphate sulphur is determined by extraction of coal with dilute hydrochloric acid. 5 gm of coal (100 mesh) is digested with 300 c c of 3% hydrochloric acid for 40 hours at about 60°C A higher temperature would cause the sulphur to escape as sulphuretted hydrogen gas The solution is then filtered and the sulphur precipitated by the barium chloride method

A certain amount of organic sulphur could be leached by phenol and pyridine treatment but complete removal of organic sulphur was not effected by such organic solvents The amount of organic sulphur was therefore obtained by difference

The total sulphur in coal was determined by following the usual Eschka method.

In the hand specimens of many of the Tertiary coals of India patches, granules and lumps of pyrite are often easily detected. When occurring as fine disseminations in coal it may escape detection by the naked eye but when such coal is exposed to moist air for some time the pyrite gets decomposed and altered to ferrous sulphate During this process increase in volume takes place and the coal usually is fissured and reduced to powder Such a change is often observed in museum specimens exposed to humid climate

In the Gondwana coals of India pyrite and marcasite are found to occur in very small patches and the sulphur content is usually very low as compared to that of the Tertiary coals of India

In the case of pyrite occurring in big lumps and granules, conditions may sometimes be favourable for their removal by mechanical washing arrangements but this process would not be successful when there is very fine disseminations of pyrite.

When coal is burnt, *i e* during the process of combustion, pyrite is decomposed and sulphur is oxidised to SO_2 and subsequently to SO_3 and finally to sulphuric acid This is why the sulphur bearing coals when burnt on the grates give off sulphurous smoke and the metallic parts of the boiler get easily corroded and damaged. When coal seams containing pyrite are exposed to humid atmosphere in mines pyrite is gradually oxidised and converted to ferrous sulphate with the formation of some amount of sulphuric acid. This is why the percolating water accumulating in the sump is generally acidic and the pumping machinery including the pipes get corroded and damaged

High volatile pyritous coals when subjected to process of high temperature carbonisation give off sufficient sulphurous smoke and the gas that is obtained has always to undergo purification process if it is to be used for town lighting and other domestic purposes If such coal happens to be of good quality caking type the coke obtained by high temperature carbonisation usually retains a certain amount of sulphur and the coke is thus rendered unsuitable for being used in the smelting operations It has been found that pyrite in the coal on combustion is completely decomposed and the sulphur is eliminated as SO_2 to be finally oxidised to sulphurous and sulphuric acids, iron being converted to oxide or silicate as the conditions prevail

Sulphur in the shape of sulphate of iron, calcium, aluminium, etc , sometimes occurs in coal specimens and usually remains in the ash after complete combustion and may thus be regarded as an inert form of sulphate sulphur The only deteriorating effect of this form of sulphur is that it will absorb some amount of heat during combustion This sulphate sulphur is generally found to occupy the joints and cleats and the planes of laminations showing that this might be due to process of secondary infiltration It may however form a part of the original inorganic matter which on combustion gives rise to inherent ash It has been found that during combustion the sulphate sulphur suffers very little change and usually remains as an inert sulphate in the ash

While dealing with Tertiary coals of N W India and Assam it was found that the amounts of total sulphur in many of them were much higher than the ash contents as shown in Table I This feature attracted the notice of the present author who advanced a suitable explanation in a previous publication [4]

TABLE I

	Mach	Watching	Borjan	Tipong Pani	Namdang	Cherrapunji	Laitringow	Thangnat
Ash %	2 32	0 42	3 03	3 92	0 69	2 76	3 65	2 43
Total sulphur %	3 95	5 10	3 75	5 11	3 01	3 18	3 78	3 91

On laboratory investigation of clean and fresh specimens (see Table IV) it was found that the pyritic sulphur content in the coals was very small compared to the total sulphur content. The coals, however, possessed a very low amount of ash. The major portion of the sulphur was found to be in an organic state of combination This interesting feature can be explained by the assumption that the original vegetable mother substance was of great purity in the first place and during the time of deposition it was not mixed up or contaminated with large amounts of dirt or impurities, nor were the coal seams, after they had been deposited, traversed by percolating water charged with iron or other salts. The sulphur deposited in the coal seam was in various organic compounds which on burning leaves no ash. This accounts for the low ash and high sulphur content of these coals. This organic form of sulphur was apparently formed and deposited in the coal during the process of coalification including biochemical changes and bacterial activity and the source would be in the original mother substance together with the remains of sulphur secreting organisms. It was pointed out by Anderson Roberts[5] that the presence of sulphur in the coal acid was a definite proof of the existence of organic sulphur in the coal. In support of the suggestion now made by the present writer some evidence in the shape of laboratory investigations may be cited Clean, fresh and unaltered pieces of Watching and Namdang coal of Upper Assam were carefully selected and particular attention was given to remove any trace of visible pyrite granules or patches These specimens on analysis were found to contain very small amounts of pyritic and sulphate sulphur whereas organic sulphur was present in sufficient amount The ash content in either case was well below 1% whereas the total sulphur was 5% and 3% respectively for Watching and Namdang coals The specimens of these coals were allowed to remain in the museum under humid Calcutta climate for a number of years and after careful re-examination the coal fragments appear to have remained very fresh and have retained the same lustre as before No pyrite patches were visible nor could any amount of sulphate be detected on close examination The coal pieces have thus suffered no crumbling due to decomposition and oxidation of pyrite The coal has in other words withstood the weathering remarkably well A reference to analytical Table IV will show that these two specimens under examination contain small amounts of pyritic and sulphate sulphur On being exposed to humid conditions for a long time all the pyritic sulphur should have been completely converted to sulphate and as a result of this alteration the value of sulphate would have been much greater in the weathered specimens On re-examination a slight increase in sulphate has been noticed but complete oxidation and alteration of pyrite has not resulted It may be said by way of explanation that as the coal is compact and as the pyrite occurs in very small granules and is interspersed in the coal substance it had escaped weathering Only those few granules that came in contact with the atmosphere were oxidised to sulphate On the other hand, other pyritous coal specimens on being subjected to similar weathering process have been completely reduced to powder with the formation of sulphate efflorescence products The specimens on careful analysis appear to have retained the same amount of total sulphur This shows conclusively that the major portion of sulphur is in an organic state of combination and is hence not affected by weathering The organic sulphur compounds on combustion get completely decomposed and leave behind no ash This may be considered to be the satisfactory explanation why we find in these coals a high percentage of sulphur irrespective or independent of low ash content This would indicate that by any mechanical means of washing the organic sulphur cannot be removed and as there is a sufficient amount of organic sulphur in many of the Tertiary coals of India installation of washing plants will not prove very successful in eliminating all the sulphur content from the coals. Only the big lumps and granules of pyrite might be removed by such a process of washing or under more favourable conditions by hand-picking. During the process of coal combustion the organic sulphur is completely decomposed and is given out as SO_2 in the product of combustion and will thus produce a corrosive effect on the metallic parts of boilers and other steam-raising plants

The forms in which sulphur generally exists in coal are therefore (i) pyritic, (ii) sulphate, (iii) organic, and (iv) free When coal is carbonised or burnt these different forms of sulphur behave differently and are split up into forms which we record as (i) fixed sulphur, (ii) volatile sulphur, (iii) combustible sulphur, and (iv) non-combustible sulphur It may be mentioned that the mere knowledge of the presence of organic, pyritic and sulphate sulphur in coal does not help the coal consumer to the fullest extent and his decision regarding proper selection of coal will not be satisfactory unless the amounts of fixed sulphur, volatile sulphur, combustible sulphur, and non-combustible sulphur are taken into proper consideration In the following lines an explanation of these sulphur forms and their scope and bearing on industries is given

(i) ***Fixed sulphur.*** It is the amount of sulphur retained by the coke when the coal is carbonised This is a very important factor to the metallurgists and iron smelters A metallurgical coke containing a high percentage of sulphur is not considered to be suitable for iron blast furnaces and other high class smelting operations. Some of the high grade caking coals of Upper Assam with the least possible ash and high volatile matter are excluded from high class metallurgical work on account of their high fixed sulphur content.

(ii) *Volatile sulphur:* It is the portion of sulphur which volatilises when the coal is carbonised at 950°C. for the determination of volatile matter It will consequently vary with the variation of temperature of carbonisation. The volatile sulphur is a guide to the sulphur content of the gaseous and liquid products obtained from the coal When this sulphur content is high the gaseous and liquid products will have to be further purified to get rid of the sulphur that is in excess of specified limit and this will naturally involve extra cost. It may be mentioned here that a certain amount of volatile sulphur may thus be recovered in the gas and other industries and may be subsequently utilised for the manufacture of sulphuric acid.

(iii) ***Combustible sulphur:*** This is the sulphur that is expelled during the complete combustion of coal. The combustible sulphur, however, includes the total amount of volatile sulphur. When present in appreciable amount in coal, this combustible sulphur corrodes the metallic structures of boilers. This item concerns the fuel engineers using coals for their different types of boilers and other steam-raising plants. Attempts should, however, be made to recover the combustible sulphur from the products of combustion in various factories and power-generating stations and may thus be utilised for our use.

(iv) ***Non-combustible sulphur:*** This is the sulphur left in the ash after the coal is completely burnt. This sulphur is considered to be inert in its activities.

The present writer made a quantitative determination of the various sulphur forms occurring in several specimens of Tertiary coals of India and Burma[6] and some of the results are shown in Table IV The author has also discussed the question of proper utilisation of these coals in the light of sulphur contents

Some of the Upper Assam coals having a high percentage of fixed sulphur were carbonised at high temperature (950°C) and an attempt was made to find out how the forms of sulphur were redistributed in the resulting coke

Regarding the estimation of the different forms of sulphur in coke the usual methods mentioned by the author have been adopted and the results are already published[7] For the determination of sulphide sulphur a method similar to that used by Bradbury[8] and described by Parr[9] has been followed and the nature of the sulphur forms studied About 2 grams of powdered coke are placed in a flask and about 150 c c HCl (1 1) poured into it and a stream of hydrogen gas is allowed to bubble through the liquid The gas evolved is allowed to pass through a flask containing a saturated solution of sodium peroxide which will absorb any sulphuretted hydrogen that evolves from the coke The content of the flask is next brought to boiling for half an hour and after these reactions are over the contents of sodium peroxide solution are tested for the presence of sulphide sulphur by the barium chloride method The substance remaining in the flask containing coke and hydrochloric acid solution is next filtered and washed and the solution tested for the presence of sulphate sulphur in coke by the barium chloride method The residue of this extraction is then treated with conc nitric acid for two hours or more in order to extract any pyrite which might remain and it has been found in all cases that no trace of pyrite could be detected

The finely powdered coke, which is boiled with dilute HCl to release the sulphide sulphur as H_2S, is further subjected to the action of nascent hydrogen in presence of dilute HCl at some elevated temperature Under these conditions some amount of H_2S is removed and the action of nascent hydrogen on the coke indicates the organic nature of the coke sulphur The organic form of resinic sulphur is not found to be present in the coke as no sulphur could be extracted from coke by means of pyridine

From a careful study of the laboratory investigations as given in Table II it is believed that the major portion of coke sulphur is present in some unknown form Formerly it was difficult to conceive any organic sulphur compound withstanding the high temperature of caking process and the development of a more stable inorganic form during the process was considered a more probable explanation The treatment of the coke residue with HCl and HNO_3 in various ways has however failed to extract all of these sulphur contents. It is suggested that during the caking process secondary reactions taking place between the complex coal constituents and the decomposed sulphur compounds may be responsible to some extent for the quantity of sulphur in stable form which is retained by coke.

TABLE II

%	Coal	Coke	Coke from coal washed with HCl	Coke acted on by hydrogen	Coke acted on by nascent hydrogen
NAMDANG					
Total sulphur	3 01	2 56			
Volatile ,,	1 58				
Fixed ,,	1 43				
(Sulphur in coke)		2 56	2 48	2 56	2 56
Sulphide sulphur	0 00	0 03	0 03	0 06	0 10
Pyritic ,,	0 03	0 00	0 00	0 00	0 00
Sulphate ,,	0 02	0 016	0 00	0 016	0 016
Organic ,,	2 66	0 00	0 00	0 00	0 00
Unknown ,,	0 00	2 51	2 45	2 48	2 44
WATCHING					
Total sulphur	5 10	4 11			
Volatile ,,	2 82				
Fixed ,,	2 28				
(Sulphur in coke)		4 11	3 60	4 11	4 11
Sulphide sulphur	0 00	0 08	0 08	0 12	0 25
Pyritic ,,	0 43	0 00	0 00	0 00	0 00
Sulphate ,,	0 04	0 03	0 00	0 03	0 03
Organic ,,	4 54	0 00	0 00	0 00	0 00
Unknown ,,		4 00	3 52	3 96	3 83
TIPONG PANI					
Total sulphur	5 11	3 72			
Volatile ,,	3 00				
Fixed ,,	2 11				
(Sulphur in Coke)		3 72	3 45	3 72	3 72
Sulphide sulphur	0 00	0 10	0 10	0 11	0 24
Pyritic ,,	0 13	0 00	0 00	0 00	0 00
Sulphate ,,	0 05	0 02	0 00	0 02	0 02
Organic ,,	4 40	0 00	0 00	0 00	0 00
Unknown ,,		3 60	3 35	3 59	3 46

Regarding the occurrence of this stable form of sulphur in coke the various possibilities were discussed by Parr It may be mentioned that in the case of the specimens under investigation nitric acid could scarcely extract any sulphur from coke showing that all the pyritic sulphur had completely decomposed. Treatment with different reagents including HF did not however release any H_2S. These considerations together with the results of nascent hydrogen treatment suggest the probability of some form of organic sulphur compound the definite nature of which has yet to be understood. It is however a well-known fact that nitrogen, sulphur and hydrogen may remain in organic combination at very high temperature (1000°C.) as shown by liberation of NH_3 and H_2S by treating red-hot coke with water vapour.

Laboratory investigations show that during the process of caking, pyritic sulphur gets completely decomposed as no trace of it is detected in the coke. The sulphate sulphur remains more or less unchanged and is retained by the coke A slight decrease of sulphate sulphur is perhaps due to the partial reducing action of red-hot carbon on the sulphate The analytical results also show that by digesting the coal with HCl the sulphate sulphur is completely removed and that the coke obtained from this washed coal does not contain any sulphate sulphur Regarding the sulphide sulphur form it may be said that during caking this form of sulphur gets slightly developed Some experiments were carried out by the author to find out the possible nature and source of this sulphide sulphur A portion of the coal was digested and washed with HCl to get rid of any sulphate sulphur and the washed coal was subjected to high temperature carbonisation and the resultant coke was analysed and the results given in Table II show that the coke from washed coal contains some amount of sulphide sulphur Another portion of the coal that was washed with dil HCl was further treated with an organic solvent like pyridine to get rid of organic resinic sulphur and subsequently subjected to caking process The coke thus obtained was subjected to chemical treatment and was found to release a small amount of sulphide sulphur These results indicate that the sulphide sulphur does not originate from sulphate or resinic organic sulphur but possibly from some other stable form of sulphur during the process of caking, the organic nature of which has yet to be properly understood.

Regarding the proper utilisation of the different coal samples, attention should always be given to the amount of the different sulphur forms in them It is a well-known fact that a large amount of combustible sulphur in coal will have a corrosive action on the metallic structures of boilers and steam raising plants and that coal having a high percentage of fixed sulphur (1·5% or more) cannot be recommended for the manufacture of metallurgical coke suitable for blast furnaces and other high class smelting operations It may however be noted that the above-mentioned high volatile coals of Upper Assam with low ash percentage may be tried as pulverised fuel or may be used for the manufacture of gaseous fuel In the latter case the sulphur may be recovered from the gas during the purification process and utilised for the manufacture of sulphuric acid. As there is an appreciable amount of organic sulphur it will not be possible to get rid of all the sulphur by any mechanical process of washing. In support of this an experiment was carried out on a small laboratory scale when the clean and unaltered Namdang coal after washing was found to retain almost the whole amount of sulphur which was afterwards found to be mostly in an organic state of combination The author however suggests that the sulphur content in the high grade coals may be reduced to some extent by mixing or blending with other varieties of coal or coke dust with lower sulphur content so that the blended coal may be a slightly better fuel The ratio of such blends has to be determined by trials The attention of the colliery proprietors and mining engineers is drawn to this suggestion for further investigation The high sulphur coals may better be utilised in the ovens and kilns where the flame does not come in direct contact with any metallic structures In coals having low ash and low pyritic sulphur there will be little chance for the formation of fusible silicates or clinkers in the ash In the case of some Upper Assam coals with a high amount of volatile matter and very low ash content the writer suggests that the different coal samples may be utilised as colloidal fuel (petroleum being easily available in the locality) so that a certain amount of petroleum might be reserved and coal might in turn be better utilised

Formerly the high percentage of sulphur in the Tertiary coals of India was thought to be chiefly due to the presence in them of iron pyrite and the total sulphur alone used to be determined It has now been found from the investigations of the present author that a coal with high total sulphur may have only a very small amount of pyrite in it and this high sulphur content may be due chiefly to the organic form

In conclusion the author desires to draw the attention of the coal producers and coal consumers to the fact that the total sulphur is not the only criterion which should form the basis of selection of coal but that the different forms of sulphur in coal should be determined before a particular high sulphur coal is recommended.

In Table III the results of proximate analyses of some of the Tertiary coals of India are given and Table IV shows the amounts of different sulphur forms in them The method of proximate analysis adopted in the laboratory has already been discussed in a previous communication [10]

Explanation of Table IV.

The values of different sulphur forms are given in percentages of coal Total sulphur is determined separately Fixed sulphur is the amount of sulphur in coke calculated in terms of coal This fixed sulphur together with volatile sulphur forms the total sulphur Non-combustible sulphur is the amount of sulphur in ash calculated in relation to coal The non-combustible sulphur and the combustible sulphur together form the total sulphur Pyritic, sulphate and the organic sulphur determined separately all go to make up the total sulphur.

TABLE III (*Proximate Analyses*)

%	Watching	Borjan.	Tipong-Pani.	Namdang	Cherra-punji	Laitrin-gow	Thangi-nat	Mach.	Maker-wal	Dandot	Jammu
Moisture	6 31	4·60	2 45	2 05	1 96	1 75	1 44	10 83	3 78	5·09	0 83
Volatile Matter	39·16	48 91	41 52	41 95	43 70	42 00	36 64	40 57	49 79	43 41	14 40
Ash	0·42	3·03	3 92	0 69	2 76	3 65	2 43	2 32	10 00	12 10	12 11
Fixed carbon	54 11	43 46	52 11	55 31	51 58	52 60	59 49	46 28	36 43	39 40	72 66
TOTAL	100·00	100 00	100 00	100 00	100 00	100 00	100 00	100 00	100 00	100 00	100 00
Colour of ash	Light Pink.	Deep Pink	Pink.	Faint Pink	Pink	Buff	Brick Red	Light Red	Light Pink.	Brick Red	Cream
Nature of coke residue.	Slightly Caking	Caking	Strongly caking	Very strongly caking	Strongly caking	Strongly caking	Strongly caking	Caking	Caking	Caking	Strongly caking

TABLE IV (*Sulphur Content*)

%	Watching	Borjan	Tipong-Pani	Nam-dang	Cherra-punji	Laitrin-gow	Thangi-nat	Mach	Maker wal	Dandot	Jammu.
Total sulphur	5 10	3 75	5 11	3 01	3 18	3 78	3 91	3 95	4 61	9 08	1 94
Fixed ,,	2 28	1 66	2 11	1 43	1 66	1 48	2 02	1 74	1 55	4 77	1·08
Volatile ,,	2 82	2 09	3 00	1 58	1 58	2 30	1 89	2 21	3 06	4 31	0 86
Pyritic ,,	0·43	0 90	0 13	0 03	0 20	0 14	0 295	0 42	1 15	5 46	1 02
Sulphate ,,	0·04	0 12	0 05	0·02	0 015	0 06	0 08	0 36	0 03	1 60	0 11
Combustible sulphur	5·05	3 39	5·05	2 96	3·02	3 74	3 86	3 77	4 53	8 91	1 91
Non-combustible ,,	0·05	0 36	0·06	0 05	0 157	0 037	0 05	0 18	0 08	0 17	0 03
Organic sulphur	4 54	2·60	4 40	2 66	2 96	3 57	3 53	3 15	3 41	1 98	0 81

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MOISTURE IN COAL

By E. R. GEE, *M.A.* (*Cantab.*), *F.G.S.*, *Geological Survey of India*

That coal has been derived by the chemical decomposition of vegetable debris that existed during an earlier geological age is agreed at least by the vast majority of scientific workers. And although we are still very much in the dark as regards the exact chemical constitution of the resultant coaly matter certain facts regarding the nature of the processes that led to the conversion of the vegetable debris into peat, brown coals and lignites, bituminous coals, and into anthracites are at least apparent. In the very earlier stages, following the deposition of sediments over the vegetable debris, the rapid de-watering of the debris was undoubtedly the principal feature. With the increase of pressure and a rise in the temperature as a result of the increasing thickness of the overburden, chemical changes undoubtedly set in rapidly within the much-compacted mass of vegetable matter. Whether one accepts the peat—brown coal—lignite—bituminous coal—anthracite theory or not, one must at least admit that the changes involved included (1) the further gradual elimination of water as a result of both physical and chemical reactions, and (2) the elimination of oxygen, possibly as CO_2 and H_2O during chemical decomposition.

The above-mentioned changes are exemplified in the following analyses of the various members of the peat-anthracite series quoted below :—

	Irish Peat	Morwell Brown coal	Malayan Lignite	Bituminous coal (Dishergarh seam)	Welsh anthracite
Percentage H_2O in raw material	90	55	20	2.5	1.0
Percentage O_2 in dry, ashless material	32	29	20	10	4.0

The above-mentioned moisture, which is 'residual' to the original vegetable debris or the result of chemical changes taking place during the maturing of the coal, may be regarded as inherent in the coaly matter and in the mineral matter that is included in the coal. This inherent moisture, with the exception of that combined with the mineral matter, is eliminated when the coal is heated for a short period at about 105°C.

In addition to the above-mentioned 'inherent' moisture, coal is known to absorb appreciable quantities of water when exposed to a humid atmosphere, especially if the coal is in a finely divided state. Such additional moisture is likely to be absorbed in the mines, during transportation in open wagons, or

[Published August 22nd, 1940.

during washing Moisture of this type is, however, at least largely eliminated by air-drying

In view of the above chemical and physical changes during coalification it would, therefore, not be surprising to find a close relationship between the proportion of 'inherent' moisture and the degree of maturity of a coal This appears to be the case in at least many Indian coals The well-matured coking coals of the Jharia, Giridih and Raniganj fields are all low in moisture—not more than 2 per cent and very often less than one per cent (calculated on an ash-free basis) In the case of the non-caking and semi-caking coals of the Barakar measures of other fields and of the Raniganj coal measures, the moisture usually varies from about 3 to as much as 10 per cent

A study of the composition of the coals of the Raniganj field and of certain of the Barakar coals of Jharia and Giridih shows that the caking properties of these coals are also definitely related to their oxygen contents, calculated on a moisture-free basis This relationship has been recognised in the case of other countries

It is found that the hard-caking coals of the Barakar measures, which are, as above-mentioned, low in moisture, are relatively low in oxygen—less than 8 per cent calculated on the dry, ash-free basis The Sanctoria and Dishergarh seams of the Lower Raniganj measures, which yield a fairly hard, vesicular coke on carbonisation, usually contain from 1 75 to 3 0 per cent moisture and an oxygen content of about 9 5 to 11 per cent, whilst the poorly-caking and non-caking seams contain higher percentages of moisture and oxygen percentages of about 11 5 to 14 This relationship is well-illustrated when we trace the change in the Sanctoria-Ponitati seam across the Raniganj field, from the relatively low moisture, caking coal of the Sanctoria-Sitalpur area to the less strongly caking coal of the Charanpur-Shripur area, into the non-caking or very poorly caking, high moisture coal of the Damodarpur-Akholpur area This seam, and also others in the field, affords an excellent example of a coal seam showing considerable change in chemical composition, laterally

It appears therefore that the moisture content of at least a number of Indian coals is closely related to the rank of the coal—that is, to its degree of maturity. As the coal increasingly matured giving rise to low oxygen caking constituents, so at the same time the inherent moisture was being gradually eliminated as a result of the chemical changes that took place.

In addition to the moisture present in the combustible element of coal, there is also the water of combination that occurs in the various hydrated minerals which comprise the mineral matter. This water of hydration is usually not eliminated at the temperature of 105°C to which the sample is normally heated in order to determine the 'proximate moisture' In some cases it is necessary to heat the mineral matter to temperatures of 300°–500°C. before this water is driven off. The amount of H_2O in question is obviously not sufficient to make any appreciable difference to the total 'proximate moisture' of a particular sample but in the case of accurate ultimate analytical work, when dealing with inferior coals containing say over 20 per cent of mineral matter, this water of hydration may well affect the determination of hydrogen (and oxygen) It might, therefore, be necessary to de-ash such coal samples as far as possible by dissolving out the mineral matter with acid (hydrochloric and hydro-fluoric) prior to determining the carbon and hydrogen

There is one other point I would like to mention, namely the percentage of moisture that is absorbed by smokeless fuel in India during the monsoon period When burning smokeless fuel in England, the difference between its ignition temperature during the dry months as compared with the wet winter periods was very marked During the former, the fuel ignited without difficulty whilst during the latter it was necessary to mix it with coal or wood in order to get it to burn satisfactorily Possibly, the question has been investigated in India It is, I think, a point of some practical importance in connection with the question of increasing the popularity of such fuel in this country, for during the monsoon season there is the possibility of these soft cokes absorbing appreciable quantities of water, during transport and delivery, and so becoming very difficult to ignite

A CRITICAL STUDY OF SOME INDIAN COAL ASHES

By R K Dutta Roy, *M Sc*, *Dr Ing*, *Geological Survey of India*

In coal, the mineral matter, which gives rise to the ash when the coal is burnt, may be generally classified as inherent and extraneous impurities The former is derived either from the inorganic salts of vegetation from which the coal was formed or from dust or sludge carried and deposited by wind and rain The latter represents partings, bands or nodules of pyrite, shale and calcite, etc In consequence, the coal ash consists mainly of silicates, sulphates, phosphates, alumina, lime, magnesia, oxide of iron and alkalies It also contains traces of Cobalt, Nickel, Silver, Barium, Zinc, Lead, Cadmium and rare elements.[1]

From the commercial and industrial point of view, the quantity, composition and the fusibility of ash in coal are of considerable importance It is an imperative necessity both for the metallurgist and the fuel-engineers to be well conversant with the characteristics of fuels that are going to be consumed either for metallurgical operations (such as blast-furnace or foundry) or for boilers and gas-producers When selecting coke for the blast-furnace or the foundry, it is of considerable importance for the metallurgist to consider the ash-content and the composition of the ash of the coke along with other important properties of coke such as porosity, hardness, combustibility and uniformity of the size, etc The serious disadvantage which is met with in the blast-furnace operation due to the high ash-content in coke is well known. The high ash-content naturally diminishes the calorific value of the coke and further it necessitates the addition of lime to flux the ash and to liquefy it into slag, a certain amount of more fuel is required besides the increased blast, steam and time, etc.

Again the percentage of ash-content is not the only factor involved in the evaluation of the suitability of the coal for fuel purposes For the efficiency of the boilers and gas-producers, the fusibility of ash plays an important rôle The lower the fusion-temperature of the coal-ash, the greater is the tendency to form clinkers on the fuel-bed in the case of boilers and gas-producers. The formation of clinkers on the fuel-bed is detrimental for the following reasons.—

(I) Firstly, combustible matter becomes enclosed within the molten 'ash' which excludes air from it and the coal so enclosed passes away into the ash-pan and is thus wasted.

(II) Secondly, inefficient combustion takes place since the clinkers prevent the induction of air through the fuel-bed

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(III) Thirdly, the coal-ash may attack the refractory materials of the furnace and also cause excessive damage to the fire-bars

(IV) Fourthly, the clinkers necessitate further labour cost for cleaning the furnace

From what has been said, it is clear that a thorough study on the composition and fusibility of ash is of vital importance for determining the factors in connection with the question of fuel-economy in the Iron and Steel Industry and in boiler plants

The object of this paper is to present the results of investigations carried out on the composition of ash on the following lines —

(I) Firstly, the chemical composition and the fusibility of ash obtained by burning coal at 950°C

(II) Secondly, the chemical composition of ash obtained by burning coal at different temperatures (750°C , 850°C and 950°C)

Though comprehensive studies have been made on the physical and chemical properties of Indian coals, the work done on the composition of ashes has been very limited The *Memoirs* and the *Records of the Geological Survey of India*[1] furnish some valuable information regarding the composition of coal-ashes Recently Mazumder[2] has studied the chemical composition of ashes of 49 different samples of coal from various parts of India but he has not dealt with the fusibility of ash

THE CHEMICAL COMPOSITION AND THE FUSIBILITY OF ASH

The ash in coal is considered to be a deleterious ingredient since it is an anti-calorific substance which does not produce heat but actually absorbs heat in attaining the temperature of the fire The composition of the ash varies widely from seam to seam and the variation in the composition may sometimes occur along a particular seam 20 samples of coals have been selected for the investigation and the area from which they have been collected are as shown below:—

Jharia field .	9
Raneegunge field	9
Salt Range	1
Assam coal	1
	20

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The proximate analyses and the colours of the ashes of the respective samples are shown in Table I The analyses of ashes, which were obtained by burning coals at 950°C in an electric muffle, have been performed according to the standard methods [1] and the results are recorded in Table II

From Table I, it will be evident that the colour of the ashes varies from white to buff and it is rather interesting to find out if any relation exists between the colour and the chemical composition of the ashes The buff and reddish colour in ash is generally due to the presence of iron-pyrites and manganese Generally speaking, the colour of the ashes of coals from the Jharia field varies from white to grey while that from the Raneegunge field varies from drab-grey to buff This striking variation in colour of the ashes of the two series of coals cannot be fully explained by the difference of the iron and manganese contents Hence it is rather difficult to warrant the laying down of any definite relationship between the colour of the ash and its chemical composition

The chemical composition of ashes (Table II) reveals the fact that in general there exists no marked difference between the mineral contents of the coals of the Jharia field and the Raneegunge field The chemical composition of two Tertiary coals (one from the Salt Range and the other from Assam) differs markedly from those of the Jharia field or the Raneegunge field These contain a high percentage of SO_3 while P_2O_5 and MnO are conspicuous by their insignificant amounts This variation in composition of the ashes of Tertiary coals and of Gondwana coals of Jharia and Raneegunge fields is of considerable importance to stimulate speculations regarding the formation and origin of Tertiary coals

Having studied the chemical composition of ashes, it is of special importance to make investigations on the fusibility of ashes It has already been stated that the behaviour of ashes on melting is an important factor for the calculation of efficiency of the boiler plants or gas-producers Various mehods have been recommended for the determination of the fusion point of ash from time to time, by different investigators The methods often employed consist in moulding the ash into the form of seger-cones with some suitable material and testing them in furnaces The temperature at which the tip of the cone touches the base of the supporting material is regarded as the fusion-temperature

La Chatelier and Chantetre [2] and Cobb [3] found out the fusion-points of ashes by making balls from the ashes and heating them in furnaces Marks [4] and Rickets [5] determined the fusion-point by using the seger-cone method Later

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[1] Mellor, J. W —A Treatise on Quantitative Inorganic Analysis, (1938)
Washington, H. S —Chemical Analysis of Rocks, (1930)
Hillebrand and Lundell—Applied Inorganic Analysis, (1929)

[2] Bulletin Soc d'encour , p 273, (1902).

[3] *J. Soc. Chem. Ind.*, p. 11, (1904)

[4] *J. Am. Soc. Chem. Eng.*, p. 205, (1915).

[5] *Ibid.*, p. 213, (1915).

TABLE I.

			Seam	Moisture %	V M %	Ash %	F.C %	S %	C Index	Colour of ash.
Bhagatdih	Jharia field	Barakar Series	11 seam Sec B	0·80	24·42	15·08	59·70	0·56	18	Grey
Ena	,,	,,	11 seam bottom	1·30	24·62	14·42	59·66	0·43	17	,,
Kustore	,,	,,	12 and 13 seams	0·82	21·06	15·32	62·80	0·54	16	Cream
Kustore	,,	,,	13 seam	0·62	22·80	16·28	60·30	0·68	17	,,
Gopalichak	,,	,,	14 ,,	0·60	24·32	13·70	61·38	0·54	14	Grey
Malkera	,,	,,	15 ,,	0·90	23·60	13·80	61·70	0·57	14	White.
Sijua	,,	,,	16 ,,	0·80	24·76	18·10	56·34	0·54	18	Grey
Jamadoba	,,	,,	17 ,,	1·45	28·30	10·10	60·15	0·44	16	,,
Jamadoba	,,	,,	18 ,,	1·76	28·56	14·30	55·38	0·47	14	Pinkish white
Victoria West	Raneegunge field.	,,	Top Ramnagar	1·40	23·10	12·84	62·66	0·43	16	Salmon buff
Seetalpur	,,	Raneegunge Series	Dishergarh seam	2·00	35·40	13·27	49·33	0·23	12	Drab grey.
Aldihi	,,	,,	,,	2·00	38·20	11·82	47·98	0·28	11	,,
Dishergarh	,,	,,	,,	2·60	36·50	11·15	49·75	0·24	13	Light buff
Nega	,,	,,	,,	2·50	38·63	10·24	48·63	0·28	10	,,
Muruldih	,,	,,	Mohuda bottom	2·38	30·20	12·72	54·70	0·32	12	Drab grey
Saltor	,,	,,	Dishergarh seam	2·30	37·80	14·34	45·56	0·30	11	Light buff
Shripur	,,	,,	Pomati	2·00	37·92	10·10	49·98	0·28	11	Pinkish buff
Charanpur	,,	,,	,,	4·60	34·12	7·31	53·97	0·35	10	,,
Makerwal Colliery (Simpson's Mine)	Salt Range		Makerwal	3·04	43·43	9·24	44·29	5·65		Ecru drab
Assam Coal (Mawbel Karas)	. .			0·98	43·06	4·76	51·20	3·08		Pinkish buff

on, Sinnat and his co-workers[1] developed a method in which coal-ash was pressed through a circular orifice to form ash-rods and the fusion-points of these ash-rods were noted Fieldner, Hall and Field[2] made classical researches on the various factors that are responsible for the accurate determination of the fusion-point Of the various factors, the most important is the nature of the atmosphere in which the ash is heated In expressing the fusion-point, the oxidising or the reducing zone of the furnace used must be definitely stated The other important factors on which the fusion-point depends are the following.—

(a) the rate of temperature-increase in the furnace,

(b) fineness of ash

Recently Bunte and Baum,[3] and King, Blackie and Millot[4] have introduced some modified methods for the determination of fusion-points

The method employed here is as follows —

The ash is finely powdered in an agate-mortar—moistened with a solution of dextin and moulded into small triangular pyramids These are then allowed to dry in air and are then vertically mounted on a refractory base along with the seger-cones The air and gas entering the furnace are adjusted for regulating the atmosphere as well as the increase in temperature in the furnace The atmosphere surrounding the ash-cones consists approximately of equal parts of oxidising and reducing gases The rise of temperature per minute is not allowed to be more than ten degrees centigrade The temperature is carefully noted when the apex of the cone begins to bend by optical pyrometers and this is then compared with the seger-cones used Thus an accurate fusion-point is obtained The fusion-points of ashes along with their chemical composition are recorded in Table II.

From the results it is evident that, generally speaking, two broad generalisations can be drawn:—

(I) Firstly, the fusion-points of ashes from the Jharia field are higher than those from the Raneegunge field and tertiary coals.

(II) Secondly, the fusion-points of the ashes of tertiary coals are comparatively lower than those of Jharia and Raneegunge fields

The relationship between the fusibility and the chemical composition of ashes seems not to be of a definite character The main constituents of ash are silica, alumina and iron-oxide with small percentages of other constituents such as lime, magnesia, alkalies, etc As is well known, of these alumina has got the highest melting point, i e 1775°C and silica has a melting point of 1685°C. If alumina and silica are present alone, in the proportion in which

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[1] *J. Soc. Chem. Ind.*, 42, p. 267T–272T, (1923).

[2] *U.S. Bur. of Mines Bull.*, 129, (1918).

[3] *Gas und Wasserfach.*, 97, p. 125, (1928).

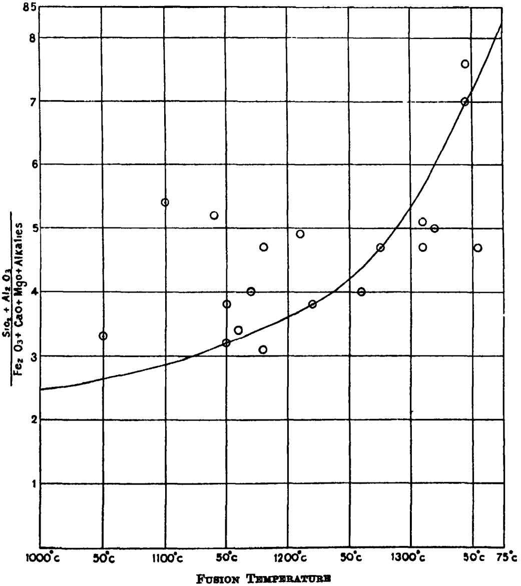
[4] *Fuel Research Technical paper* 23.

TABLE II

	Seam	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	TiO_2 %	P_2O_5 %	MnO %	CaO %	MgO %	SO_3 %	K_2O %	Na_2O %	Total	Ratio $\frac{SiO_2+Al_2O_3}{Fe_2O_3+CaO+MgO+\text{Alkalies}}$	Fusion-point of ash.
Jharia field.															
Bhagatdih	11 sec B	50 64	20 73	9 88	1 52	1 87	0 23	2 36	1 16	1 03	0 46	0 30	100 18	5 04	1320°C.
Ena	11 bottom 9′ Sec	49 74	30 71	8 43	1 42	1 32	0 32	4 56	2 02	0 80	0 43	0 20	99 95	5 14	1310°C.
Kustore	12 & 13 seams	62 64	22 15	9 20	1 42	1 20	0 02	2 10	0 34	0 30	0 54	0 49	100 40	7 00	1340°C
Kustore	13	48 34	28 12	13 80	1 50	2 36	0 32	3 20	1 08	0 66	0 46	0 60	100 54	4·00	1260°C.
Gopalichak	14	53 02	26 68	11 88	1 60	1 30	0 20	3 06	1 38	0 68	0 48	0 34	100 62	4 70	1355°C.
Malkera	15	57 60	29 20	7 20	1 32	0 53	0 12	0 82	2 50	0 48	0 58	0 30	100 65	7 60	1345°C.
Sijua	16	57 61	22 54	10 10	1 52	1 20	0 64	2 58	2 68	0 25	1 48	0 30	100 90	4 70	1310°C.
Jamadoba	17	48 24	28 22	9 73	1 42	2 30	0 15	6 30	3 10	0 42	0 42	0 34	100 64	3 84	1220°C.
Jamadoba	18	56 72	30 42	5 65	1 44	1 86	0 20	1 83	1 04	0 52	0 32	0 30	100 10	9 50	1380°C.
Victoria West	Top Ramnagar	49 40	31 48	9 20	1 20	2 30	0 13	4 22	1 60	1 10	0 80	0 60	100 03	4 93	1210°C.
Raneegunge field															
Charanpur	Poniati	55 72	27 50	9 18	1 14	0 23	Trace	2 51	2 53	0 97	0 78	0 40	100 96	5 40	1100°C.
Seetalpur	Dishergarh	51 36	23 24	11 18	1 30	1 68	0 04	6 00	4 30	0 48	0 40	0 30	100 28	3 40	1160°C.
Aldihi	,,	48 12	30 68	7 80	0 68	1 28	0 64	8 40	2 36	0 32	0 46	0 23	100 97	4 04	1170°C.
Dishergarh	,,	49 00	27 63	8 26	0 60	1 52	0 40	8 62	3 45	0 48	0 48	0 30	100 74	3 80	1150°C.
Shripur	,,	51 84	28 98	7 42	1 12	1 08	0 38	5 72	2 46	0 62	0 64	0 39	100 65	4 70	1180°C
Saltor	,,	54 18	27 42	7 20	0 70	1 68	Trace	6 32	1 42	0 52	0 42	0 26	100 12	5 22	1140°C.
Nega		46 74	27 38	10 43	1 20	1 24	0 20	8 45	2 86	0 54	0 63	0 42	100 09	3 26	1150°C.
Muruldih	Mohuda bottom	52 18	27 84	7 80	1 15	0 73	0 48	5 20	2 30	0 50	1 06	0 68	99 92	4 69	1290°C.
Salt Range															
Simpson	Makerwal	48·00	20 72	15 58	Trace	Trace	Trace	4 26	1 45	9 10	0 42	0 77	100 30	3·05	1180°C.
Assam.															
Mawbelkaras		43 04	31 40	17 89	1 38	,,	,,	1 50	1 60	2 52	1 01	0 25	100 59	3 33	1050°C.

they occur, there is practically no chance of their melting at the fuel-bed of the boilers or the gas-producers The other components such as iron-oxide, lime, magnesia and alkalies have the effect of a flux upon alumina and silica present and thus reduce the fusion-point of ash The fusion point generally varies according to the ratio between the acidic components and the bases

$$\frac{SiO_2+Al_2O_3}{Fe_2O_3+CaO+MgO+\text{Alkalies}}$$



Mean Curve showing the relation between $\frac{SiO_2+Al_2O_3}{Fe_2O_3+CaO+MgO+\text{Alkalies}}$ and the Fusion temperature.

From Table II it will be observed that this ratio varies from 9·50 to 3·05 Broadly speaking, the greater the ratio, the higher is the fusion-point

The mean curve plotted against the ratio of $SiO_2+Al_2O_3$ to $Fe_2O_3+CaO+MgO+$Alkalies and the fusion temperature of the ashes affords consistency to the above generalisations but still the departure from the mean curve cannot be overlooked Although it is not possible to draw some definite relation between the fusibility and the chemical composition of the ashes due to their complexities, the results however permit some reliable duductions to be drawn

(I) Ferric oxide, which varies from 7 to 18%, has a fluxing effect which increases almost directly to the percentage composition

(II) Lime, which varies from 0 8 to 8%, has a similar fluxing effect but the combined fluxing effect of iron-oxides and lime has a complex relation to the percentages of the two fluxes present

(III) Magnesia, which varies from 0 3 to 4% has a greater fluxing effect than lime

(IV) The alkalies are present in small amounts but their fluxing effect, in presence of comparatively high percentage of lime, is quite appreciable

(V) The ratio of silica to alumina ranges from 2 82 to 1 38 and the fusion-point generally increases with this ratio but below 1 4 it has a marked effect in decreasing the fusion-point

The function of temperature on the composition of ash

The methods, prevalent for the determination of ash-content in coal, generally consist in burning the coal at temperatures between 750°C. and 1000°C

TABLE III.

Coal.			TEMPERATURE AT WHICH COAL BURNT OFF		
			750°C Ash%.	850°C. Ash%.	950°C. Ash%.
1	Bhagatdih	Jharia field	15 48	15 32	15 08
2	Ena	,,	14 68	14 57	14 42
3	Kustore	,,	16 71	16 62	16 28
4	Gopalichak	,,	13 98	13 78	13 70
5	Kustore	,,	15 42	15 18	15 32
6	Malkera	,,	14 08	13 78	13 80
7	Sijua	,,	18 40	18 20	18 10
8	Jamadoba	,,	10 40	10 28	10 10
9	Jamadoba	,,	14 72	14 58	14 30
10	Victoria West	,,	12 91	12 80	12 84
11	Charanpur	Raneegunge field	7 80	7 62	7 31
12	Seetalpur	,,	13 60	13 40	13·27
13	Aldihi	,,	12·00	11·92	11 82
14.	Shripur	,,	10 42	10·32	10 10
15	Dishergarh	,,	11·28	11 00	11 15
16	Nega	,, .	10·40	10·32	10 24
17	Saltor	,,	14 60	14·30	14·34
18.	Muruldih	,,	12 93	12 58	12 72
19	Makerwal seam (Simpson Mine).	Salt Range .	9·98	9 61	9 24
20.	Assam Coal .	.	5·01	4 88	4·76

While expressing the results of the ash-content, the particular temperature at which the coal is burnt is not usually mentioned Therefore it seems worth while to study the function of temperature on the ash-content as well as its subsequent effect on the composition of the ash

For this purpose, three definite temperatures have been selected and the respective ashes of coals are obtained at these selected temperatures The results are shown in the Table III

From the results it will be seen that the ash-content generally diminishes with rise in temperature and the variation in ash-contents at the selective temperatures, *i e* (750°C, 850°C and 950°C), ranges from 0 40 to 0 18% in the case of coals from the Jharia and Raneegunge fields while in the case of two tertiary coals (Salt Range and Assam coals) the range lies between 0 74 and 0 25 In view of these results, it will be well to attach due consideration to the effect of temperature to the ash-content The decrease in the ash-content with the rise of temperature may be attributed to the loss sustained by the volatilisation of sulphur and alkalies

For co-ordinating the effect of temperature on the ash-content on the one hand and on the composition of ash on the other hand, a special study has been made of the chemical composition of ashes obtained at different temperatures and the results are recorded in Table IV

From the results the following conclusions may be drawn —

(I) The variation of silica and alumina contents lies within a very narrow limit

(II) Phosphorus, Titanium and Manganese contents remain practically constant

(III) Ferric oxide and lime contents increase with the higher temperature

(IV) Sulphates and alkalies generally diminish at the higher temperatures

SUMMARY AND CONCLUSION

1 Twenty coals from important areas have been investigated as to the composition, distribution and fusibility of ash

2 No definite relation between the chemical composition and the fusibility of ash could be found From the ratio of

$$\frac{SiO_2+Al_2O_3}{Fe_2O_3+CaO+MgO+\text{Alkalies}}$$

it was found that, generally speaking, the higher the ratio the higher was the fusion temperature

3. From a study of the fusion-point of ash, it is possible to predict the suitability of coals for use in boilers and gas-producers without the formation of clinkers on the fuel-bed

4 The function of temperature in the determination of ash-content as well as its effect on the chemical composition has been studied.

TABLE IV

		Temperature at which ash was made	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	FeO %	TiO_2 %	P_2O_5 %	MnO %	CaO %	MgO %	SO_3 %	K_2O %	Na_2O %	Total.
Kustore	12 and 13 seams	750°C	62 52	22 12	8 64	0 21	1 40	1 06	0 02	1 91	0 35	0 53	0 58	0 68	100 02
		850°C	62 68	22 13	8 82	0 16	1 40	1 10	0 02	1 78	0 34	0 32	0 56	0 59	100 10
		950°C	62 64	22 15	9 20		1 42	1 20	0 02	2 10	0 34	0 30	0 54	0 49	100 40
Malkera	15 seam	750°C	57 52	28 86	7 00	0 28	1 30	0 50	0 12	0 82	2 20	0 52	0 58	0 32	100·02
		850°C	57 44	29 00	7 20	0 10	1 30	0 53	0 12	0 82	2 50	0 50	0 56	0 30	100 37
		950°C	57 60	29 20	7 20		1 32	0 53	0 12	0 82	2 50	0 48	0 58	0 30	100·65
Sijua	16 seam	750°C	57 20	22 72	9 10	0 28	1 52	1 16	0 65	2 20	2 58	0 45	1 60	0 50	99 96
		850°C	57 52	22 74	9 60	0 14	1 55	1 15	0 65	2 43	2 68	0 28	1 58	0 42	100 74
		950°C	57 61	22 54	10 10		1 52	1 20	0 64	2 58	2 68	0 25	1 48	0 30	100 90
Jamadoba	17 seam	750°C	47 60	28 00	9 08	0 42	1 32	2 30	0 14	6 50	3 10	0 52	0 44	0 36	99 78
		850°C	48 02	27 89	9 45	0 18	1 40	2 28	0 15	6 30	3 10	0 50	0 40	0 36	100 03
		950°C	48 24	28 22	9 73		1 42	2 30	0 15	6 30	3 10	0 42	0 42	0 34	100 64
Victoria West Top Ramnagar		750°C	49 00	30 80	8 70	0 21	1 20	2 10	0 13	3 96	1 60	1 76	0·80	0 60	99 86
		850°C	49 10	30 76	8 83	0 12	1 20	2 30	0 13	4 20	1 53	1 72	0 78	0 60	100 31
		950°C	49 40	31 48	9 20		1 20	2 30	0 13	4 22	1 60	1 10	0 80	0 60	100 03
Charanpur	Poniati seam	750°C	55 16	27 41	8 80	0 26	1 16	0 22	Trace	2 20	2 63	1 12	0 80	0 44	100 20
		850°C	55 46	27 01	9 00	0 18	1 14	0 22	,,	2 43	2 43	1 08	0 82	0 42	100·19
		950°C	55 72	27 50	9 18		1 14	0 23	,,	2 51	2 53	0 97	0 78	0 40	100 96
Seetalpur	Dishergarh ,,	750°C	51 00	23 16	10 80	0 26	1 30	1 52	0 04	5 89	4 30	0 56	0 56	0 32	99 71
		850°C	51 18	23 20	11 00	0 12	1 30	1 58	0 04	5 92	4 20	0 52	0 52	0 32	99 90
		950°C	51 36	23 24	11 18		1 30	1 68	0 04	6 00	4 30	0 48	0 40	0 30	100 28
Aldihi	,,	750°C	47 66	30 10	7 51	0 24	0 62	1 26	0 58	8 01	2 34	0 66	0 56	0 30	99·84
		850°C	47 83	30 65	7 24	0 18	0 64	1 27	0 62	8 20	2 36	0 41	0 56	0 26	100 22
		950°C	48 12	30 68	7 80		0 68	1 28	0 64	8 40	2 36	0 32	0 46	0 23	100 97
Simpson Mine	Makerwal seam (Salt Range)	750°C	47 48	19 70	14 80	0 46	Trace	Trace	Trace	4 00	1 46	10 82	0 43	0 82	99 97
		850°C	47 62	20 10	15 10	0 21	,,	,,	,,	4 18	1 44	10 20	0 40	0 76	100·01
		950°C	48 00	20 72	15 58		,,	,,	,,	4 26	1 45	9 10	0 42	0 77	100·30
Assam Coal	Mawbelkaras	750°C	42 88	30 73	17 01	0 28	1 38	,,	,,	1 48	1 62	3 06	1 12	0 28	99 84
		850°C	42 95	31 03	17 62	0 21	1 40	,,	,,	1 44	1 64	2 85	1 20	0 30	100 64
		950°C	43·04	31 40	17 89		1 38	,,	,,	1 50	1 60	2 52	1 01	0 25	100 59

CLASSIFICATION OF COAL

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Coal comprises a series of substances the classification of which has been attempted for many decades past The need for some type of fairly widely acceptable classification has been felt for specifications in trade, for purposes of taxation and customs, and in legal disputes This paper gives a short review of the numerous attempts which have been made in this direction

Any acceptable scheme of classification should be scientific and systematic and should take into account the fundamental characters It should be easily comprehensible and applicable The criteria should be capable of quantitative measurements leaving nothing to mere opinions and personal factors Even if applied for purely commercial purposes, it should be sufficiently systematised

The earliest classification recognised the visual characters, agreeing broadly with the properties of combustion, *viz* —

Lignite or brown coal Brown to black in colour, woody structure, high moisture

Bituminous coal Black, often banded, ignites fairly easily and burns with flame and smoke Those which had a strong tendency to agglutinate on heating were called caking coal

Anthracite Black and lustrous and difficult to ignite, burns without flame

Regnault was the first to use a chemical classification He published a paper in 1837 in which he defined 5 groups on the basis of ultimate analysis (percentage of O+N)

	Per cent Mean (O+N)
Anthracite	2 62
Lean or short flame bituminous	4 47
Bituminous (smithy) coal	5 74
Long flame bituminous	8·89
Dry long flame	16 39

Hilt and others classified coal on the basis of volatile matter and coking property

The late Prof W A Bone modified the scheme of Regnault and published the revision in his well-known book on coal This is reproduced in Table 1

In a report printed in 1844, Walter R Johnson listed the coals of the United States of America in the order of the ratio of the fixed carbon to the volatile matter, which was found to have a definite relationship to the heat evolved in burning as measured by the amount of water evaporated The 'fuel ratio' had its origin then

VOL. VI—No. 3. [Published August 22nd, 1940.

TABLE 1 —*Regnault-Grüner—Bone Classification*

(Compositions given on ash-free basis.)

Genus.	Class	Chief uses	Percentage Composition			% Volatiles at 900°C	% Fixed Carbon.	Character of Carbonaceous residue
			C	H	O+N+S			
A Lignite	Non-caking		60 to 70	About 5 0	20 to 35	Above 45	Below 55	Non-coherent.
B Bituminous	(1) Non-caking, long flame	Reverberatory furnaces	75 to 80	4 5 to 5 5	15 to 20	40 to 45	55 to 60	Non-coherent
	(2) Caking, long flame	Gas-making	80 to 85	About 5 6	10 to 15	32 to 40	60 to 68	Very porous coke.
	(3) Hard coking	Coke manufacture	84 to 89	5 0 to 5 6	5 5 to 11 0	26 to 32	68 to 74	Dense coke
	(4) Hard coking short flame	Coke manufacture and steam-raising	88 to 90	4 5 to 5 5	5 5 to 6·5	18 to 26	74 to 82	Very dense coke
BC Semi-bituminous	Non-caking short flame	Steam raising	90 to 92	4 0 to 4 5	4 0 to 5 5	15 to 20	80 to 85	Weakly caking or non-coherent
C Anthracitic and Anthracite	(1) Anthracitic non-caking	Steam raising	92 to 94	3 0 to 4 5	3 0 to 4 5	8 to 15	85 to 92	Pulverulent
	(2) Anthracites non-caking	Domestic and central heating, Malting kilns.				Below 8	Above 92	

TABLE 2.—*Seyler's Classification*

(All numbers represent percentages)

	Anthracitic	Carbonaceous.	Bituminous			Lignitous	
			Meta-	Ortho-	Para-	Meta-	Ortho-
Genus	C over 93 3	93 3 to 91 2	91·2 to 89 0	89·0 to 87 0	87 0 to 84 0	84 to 80	80 to 75
Per-bituminous H over 5 8 Vol. 30 to 44			Per-Meta-Bituminous Northern Steam Coals Over 5 7 30 to 44	Per Ortho-Bituminous Cannels Over 5 7 Seldom under 36	Per-Para-Bituminous Over 5 8 Seldom under 40	Per-Lignitous Over 5 8 31 to 57	
Bituminous H 5·0 to 5·8 Vol. 23 to 30		Pseudo-Bituminous	Meta-Bituminous Welsh coking coals	Ortho-Bituminous Durham coking coals Smithy and gas coals	Para-Bituminous Gas and coking and free-burning steam coals. 5 0 to 5 8 30 to 40	Lignitous 4 7 to 5 8 31 to 57	
Semi-Bituminous H 4·5 to 5·0 Vol. 16 to 23		Semi-Bituminous Generally coking steam coals Over 4 45 14 to 24	Sub-Meta-Bituminous Continental coking coals 4 5 to 4 9 16 to 23	Sub-Ortho-Bituminous Westphalian coking coals 4 5 to 5 0 16 to 23	Sub-Para-Bituminous 5 0 and under 16 to 29	Sub-Lignitous	
Carbonaceous H 4·0 to 4·5 Vol. 10 to 16	Semi-Anthracitic. Non-coking, dry steam coals Over 4 9 to 15	Ortho-Carbonaceous Welsh smokeless, slightly coking coals. 4 2 to 4 5 10 to 14	Pseudo-Carbonaceous (Sub-Meta-Bituminous) steam coals 3 7 to 4 5 10 to 16	Pseudo-Carbonaceous (Sub-Ortho-Bituminous) Over 4 5 Over 16	Pseudo Carbonaceous (Sub-Para Bituminous)	Sub-Lignitous	
Anthracitic H below 4·0 Vol. under 10	Ortho-Anthracite True anthracites Below 4 0 5 to 9	Pseudo-anthracite (Sub-Carbonaceous) Dry Steam coals Bastard anthracites Below 4 2 Under 7 7	Pseudo-anthracitic (Sub-Meta-Bituminous) Below 3 7 Under 10	Pseudo-anthracitic (Sub-Ortho-Bituminous)	Pseudo-anthracitic (Sub-Para-Bituminous)		

P Frazer (1887) used the fuel ratio on the lines followed by H D Rogers a few years previously His divisions were —

	Fuel ratio
Dry anthracite	100—12
Semi anthracite	12— 8
Semi-bituminous	8— 5
Bituminous	5— 0

As this was based on Pennsylvania coals, no coals of lower rank than bituminous were considered

C A Seyler, after an intensive study of South Wales coal, drew up a classification in 1901, in which he made use of ultimate analyses The analyses were reduced to a 'pure coal' basis, i e , C, H, O and N making up 100 His investigations showed that the hydrogen content and volatile matter bore some relationship of the type

$$H = a+b \log V M \text{ (both H and V M on pure coal basis)}$$

Coals with over 84 per cent C were grouped into three genera called anthracite, carbonaceous and bituminous The bituminous coals were subdivided into three—meta-, ortho- and para-bituminous Those with C 75–84 per cent were called lignitous Those with over 84%C were regrouped into genera according to the percentage of hydrogen When the oxygen was not high, the recurrence of hydrogen percentage in different groups produced coals with closely resembling characters Seyler's classification is given in Table 2

Marius R Campbell, a great authority on coal in the United States Geological Survey, proposed a classification in 1904 based on the ratio of C to H, as shown in Table 3

TABLE 3

	Class	C H ratio
A	Graphite	∞ to ?
B	Anthracite	? to 30
C	Anthracite	30 to 26
D	Semi-anthracite	26 to 23
E	Semi-bituminous	23 to 20
F	Bituminous	20 to 17
G	Bituminous	17 to 14 4
H.	Bituminous	14 4 to 12 5
I	Bituminous	12 5 to 11 2
J.	Lignite	11 2 to 9 3
K.	Peat	9 3 to ?
L.	Wood	7 2

F. F Grout in 1907 proposed a classification based on the percentage of fixed carbon in the dry, ash-free coal in the coals of higher rank, and the total carbon in those of lower rank His scheme of 1909 was as follows:—

TABLE 4.

Class	In dry ash-free coal.	
	% Fixed carbon	% Total C
Graphite	Over 99	
Anthracite	Over 93	
Semi anthracite	83 to 93	
Semi bituminous	73 to 83	
Bituminous	47 to 73	80 to 88
Sub bituminous	47 to 73	73 6 to 80
Cannel	35 to 47	73 6 to 88
Lignite	30 to 55	65 to 73
Peat	Below 50	Below 65

In 1906 S W Parr drew up a new classification based on the ratio of volatile carbon to total carbon expressed as a percentage The volatile carbon was the difference between the total carbon and the fixed carbon (C—F C = V C) The basis of the classification was therefore $\frac{V\,C}{C} \times 100$ For lower rank coals the percentage of inert volatile matter was used and this, in the pure dry coal, was got by subtracting from 100 the percentages of C, S, ash, H_2O and available H, and multiplying the remainder by

$$\frac{100}{100-(\text{Ash}+\text{moisture})}$$

In 1922, Parr published a revised classification making use of his 'unit coal', which was again revised in 1928 Parr's unit coal is pure coal He used the following formulae —

$$\text{Unit B T U} = \frac{(\text{Indicated B T U} - 50S) \times 100}{100-(1\ 08\ \text{Ash}+0\ 55S)}$$

$$\text{Unit Volatile matter} = \frac{[\text{V M as determined}-(0\ 08\ \text{Ash}+0\ 4S)]10}{100-(1\ 08\ \text{Ash}+0\ 55S)}$$

In Parr's scheme the percentage of unit volatile matter is useful in the higher rank coals whereas the unit calorific value (unit coal B T U) is the characteristic property of the lower rank coals, which will be seen from Table 5

TABLE 5.—*Parr's classification*

Class	% unit V M	Unit coal B T U
Anthracite	0– 8	15,000–16,500
Semi anthracite	8–12	15,000–16,500
Bituminous A	12–24	15,000–16,500
Bituminous B	25–50	15,000–16,500
Bituminous C	30–55	14,000–15,000
Bituminous D	35–60	12,500–14,000
Lignite	35–60	11,000–12,500
Peat	55–80	9,000–11,000

O C Ralston (1915) calculated a large number of ultimate analysis to the 'pure coal' basis so that C, H and O totalled up to 100 He plotted the percentages of these on triaxial co-ordinates and found that the coals separated on the graphs into some natural groups

J D Fisher (1927) used two sets of trilinear co-ordinates In one he plotted the constituents fixed carbon, volatile matter and moisture, based on the ash-free coal with moisture as mined In the second were plotted C, H, O

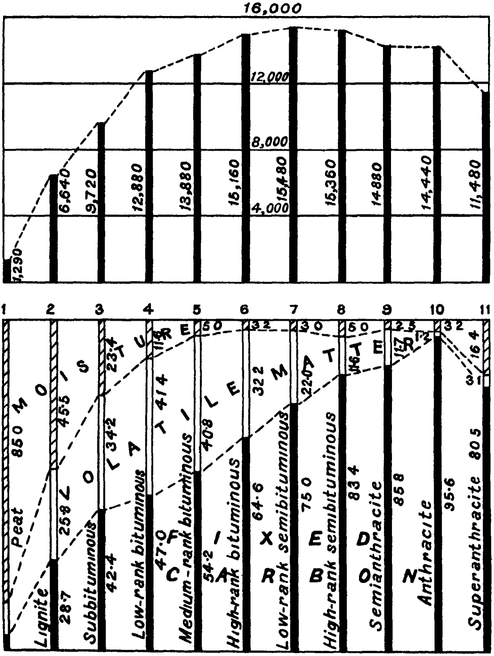

FIG. 1. *Upper diagram* Calorific values of different ranks of coal.
Lower diagram : Composition of different ranks of coal on ash-free basis.
(After M. R. Campbell.)

which were also on the ash-free, moist coal The approximate limits of the classes were shown in his diagrams by lines

E Stansfield (1925), in his investigation of coals of the Province of Alberta in Canada, found that moisture must be taken into account for a satisfactory classification There is always some difference between the ash and the total mineral matter which must also be taken into account The analyses were recast to a uniform 10 per cent ash (or 11 per cent mineral matter) which procedure was found to be more satisfactory than calculation to the hypothetical 'pure coal' basis

M R Campbell has described the classification adopted by the U S Geological Survey in a paper presented before the International Bituminous Coal Conference at Pittsburgh in 1926 The details of this are shown in the following statement (Table 6) as well as in figure 1

TABLE 6 —*U S G S Classification*

Peat —Contains approximately 85% moisture, 10 4% volatile matter, 4 6% fixed carbon, 1,290 B T U

Lignite —Brown, woody or composed of finely divided plant tissues, or amorphous and representing the first stage in the development of cannel Contains 25 to 45% moisture, on drying shrinks and breaks up in an irregular manner, 6,000 to 7,500 B T U

Sub-bituminous —Black in colour, 12 to 25% moisture, slacks on exposure, 7,000 to 11,000 B T U

Bituminous —Slacks little on exposure, 11,000 to 15,000 B T U Fuel ratio below 2 5, this class includes cannels, some of the best steam coals and the best gas and by-product coals

Semi-bituminous —Nearly smokeless, usually friable and slacks easily, 12,000 to 15,400 B T U Fuel ratio 2·5 to 5

Semi-anthracite —Harder than bituminous, burns with a short yellow flame at first and then with a blue flame; fuel ratio 5 to 10

Anthracite —Hard, burns with a blue flame, does not soil the hands, difficult to ignite but burns without smoke Fuel ratio over 10

TABLE 7.

Grade	Low Volatile.	High Volatile
Selected	Up to 13% ash, over 7,000 cal	Up to 11% ash, under 6% moisture, over 6,800 cal.
First	Up to 15% ash, over 6,500 cal	Up to 13% ash; under 9% moisture; over 6,300 cal
Second	Up to 18% ash, over 6,000 cal	Up to 16% ash; under 10% moisture; over 6,000 cal.
Third	Inferior to the above.	

A simple classification is used by the Indian Coal Grading Board (Table 7) for coal intended for export This has been in use for over a dozen years

The latest scheme evolved in America is that tentatively adopted by the American Standards Association (A S T M) This recognises four broad classes Anthracite, Bituminous, Sub-bituminous and Lignite This scheme is shown in Table 8

TABLE 8 —*Classification of coal by rank (A S T M)*

Class	Group	Fixed Carbon or B T U on mineral matter free basis	Physical property
I Anthracite	1 Meta-anthracite	Dry F C 98% or more	
	2 Normal anthracite	Dry F C 92% or more up to 98%	
	3 Semi anthracite	Dry F C 86 to 92%	Non agglutinating [1]
II Bituminous	1 Low volatile	Dry F C 77 to 86%	
	2 Medium volatile	Dry F C 69 to 77%	
	3 High volatile A	Dry F C less than 69%, moist B T U 14,000 or more	
	4 High volatile B	Moist B T U 13,000–14,000 [2]	
	5 High volatile C	Moist B T U 11,000–13,000 [2]	Either agglutinating or non-weathering
III Sub bituminous	1 Sub bituminous A	Moist B T U 11,000–13,000 [2]	Both weathering and non agglutinating
	2 Sub bituminous B	Moist B T U 9,500–11,000 [2]	
	3 Sub bituminous C	Moist B T U 8,300–9,500 [2]	
IV Lignite	1 Lignite	Moist B T U less than 8,300	Consolidated
	2 Brown coal	Moist B T U less than 8,300	Unconsolidated

[1] If agglutinating, classify under Low volatile bituminous

[2] Coals having 69 per cent or more fixed carbon on the dry mineral matter free basis are to be classified according to F C regardless of B T.U.

In the above classification the mineral matter is taken as 1 1 times the ash, which has been found to be a very good approximation to the truth Coals having calorific value of 14,000 or over on the moist mineral matter free basis and those having 69 per cent or more of fixed carbon on the dry basis are classified according to fixed carbon If the fixed carbon is less than 69 per cent on the dry basis, the classification is made on the moist B T U In some semi-anthracites it happens that they are agglutinating, in which case they will be put under the low volatile bituminous group The agglutinating test adopted is 500 grams of coal at a ratio of 15 parts of sand to 1 part of coal by the United States Bureau of Mines method

The A S T M Committee recommended the following —

$$\text{Dry mineral matter free basis} = \text{F C} \times \frac{100}{100-(\text{M}+1\ 1\text{A}+0\ 1\text{S})}$$

$$\text{Moist mineral matter free basis} = \text{F C} \times \frac{100}{100-(1\ 1\text{A}+0\ 1\text{S})}$$

For the weathering test, the United States Bureau of Mines test as described in the Report of Investigations No 3055 (1930) is applied In non-weathering coals the weathering index should not exceed 5%

Seyler has very recently published a further elaborate discussion of classification on his pure coal basis and petrological constituents Here he examines the proposition that coals of the same elementary composition are identical in all properties Examining the relation between volatile matter and hydrogen, he proposes a law similar to Dulong's law ($V = a\text{H} - b\text{C} + \text{K}$) This is found to be applicable only to bright, non-anthracitic coals He also finds that the composition of bright coal conforms to the rank Emphasis is laid on coal petrography Unfortunately, Seyler's classification requires elaborate calculations on the data of ultimate analysis especially if the coal contains appreciable quantities of 'dull coal' and is therefore highly artificial Seyler however condemns the A S T M classification because it does not take into account the petrographical constituents, and adds—'In addition, the A S T M proposals, by the unfortunate step of introducing in different parts of the same classification a change from the dry to the moist mineral free basis, destroy all the simple correlations between elementary composition, volatile matter, petrological composition and properties which we have discussed in the paper'

It will be noted that in Parr's scheme volatile matter and calorific value are used while in Seyler's the 'pure coal' is used Both these systems ignore the existence of moisture as an integral part of the coal The importance of moisture as an essential ingredient of the coal substance is now well recognised and X-ray study shows that at least in the lower rank coals it plays much the same rôle as volatile matter Hence it would seem that moisture in coal as mined (or under standard conditions of storage and drying) should be determined and taken into account for the purpose of classification

The methods of determining moisture are now far from satisfactory, whether in the raw coal as it comes out of the mine or in air-dried coal In sampling, moisture from seepage should be carefully avoided and the coal should be immediately sealed air-tight and analysed as soon as possible If the coal is stored, as is well known, moisture may be absorbed from the atmosphere or given up, according to conditions Hence the question of the evaluation of this component should be studied intensively to arrive at a satisfactory method for the determination of that part of it which is inherent in the coal

For coals of bituminous and lower ranks, the calorific value provides the best criterion for differentiation The volatile matter shows only a small variation over a wide range and there is also much overlap Similarly, the sum of volatile matter and moisture (and alternatively fixed carbon, which is simply the difference between 100 and the sum of volatiles and moisture in mineral matter free coal) fails The calorific value is, in addition, of great importance for commercial purposes and can be readily determined

The ultimate analysis of coal is particularly useful in studying the behaviour of coal of higher than bituminous rank, and has been used effectively by such authorities as Seyler and Ralston It is not so valuable in the case of the lower ranks, for, as already mentioned, there is the difficulty about moisture which these authors have completely ignored

For a classification to be of wide application, *i e* not only for one field but also over a whole country or even universally, the analytical procedure and the subsequent reduction of the results to a uniform basis should be standardised In the evaluation of mineral matter Parr has used the factor 1 08 to multiply the ash percentage Stansfield has shown that this factor varies between 1·05 and 1 20 for different Alberta coals in Canada and has advocated the use of the factor 1·1 as a satisfactory one, and the same factor has also been used by Tideswell and Wheeler and recently by the A S T M

If a standard method of adjustment is agreed upon for reduction to pure coal, comparison between different fields would be simplified Such a procedure is necessary because the collection of representative samples of high purity for 'pure coal' determination is generally difficult

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MICRO-STRUCTURE OF SOME INDIAN FUSAINS.

By N N CHATTERJEE[1]

The writer of this paper collected several samples of fusain from different coal seams and he is engaged in the physical and chemical study of them The present paper records only a part of the work and deals with the micro-structure of the following specimens —

(i) Fusain from Hurra coalfield, Rajmahal Hills
(ii) „ „ Jilbari coalfield, Rajmahal Hills
(iii) „ „ XIV seam, Jharia coalfield, Ekra colliery
(iv) „ „ Borachak seam, Raniganj coalfield
(v) „ „ Borodhemo seam, Raniganj coalfield
(vi) „ „ Salt Range coal (Ara), Punjab (kindly supplied by Dr Fox)
(vii) „ „ Talchir coalfield, Talchir colliery

Regarding the occurrence and distribution of fusain in the coal substance it may be mentioned that they occur in greater abundance in the Talchir and Rajmahal Hill coals than in the other coals of the series under discussion The Talchir and Rajmahal Hill coals are full of fusain patches which occur in a large number of thin layers When the coal specimen is split open, the surface is generally scattered over with small and thin fusain patches In the Jilbari and Talchir samples, besides fusain which occurs in a large quantity, dull coal or durain is present in a large amount and vitrain or bright coal occurs in subordinate amount In the case of Jharia and Raniganj coals fusain occurs in a small amount and in very thin layers It is very conspicuous by its softness, fibrous texture and the beautiful silky lustre on the fibrous strands As fusain has little cohesive power the coal splits readily along planes where it occurs The fusain is never found to occur in great thickness and is usually less than 2 mm thick whereas vitrain 2 or 3 inches thick and durain several inches thick have been noticed in some of the Gondwana coals The fusain is readily separated from the rest of the coal by scraping with a knife when the long fibrous strands and small sharp-pointed irregular splintery fragments fall freely from the coal specimens The Tertiary coal of the Salt Range contains only a few specks of fusain which is generally sharp-pointed, brittle and dark brownish in colour and is fairly hard at the same time

The microscopic investigation of the small samples of fusain reveals little of the structure because they are opaque Hence it is necessary to treat the material in some way to facilitate microscopic examination

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VOL. VI—No. 3. [Published August 22nd, 1940.

The simple treatment of the fusain specimens with acids as suggested by Stopes and Wheeler [1] was carried out in the author's laboratory Concentrated nitric acid together with a few drops of hydrochloric acid was added to each of the fusain specimens and left for a week The acid solutions were then neutralised by potassium hydroxide solution and after the process of neutralisation sufficient water was added to each of the specimens After the above treatment it was found that fusain in all cases forms no froth and no true solution resulted In the case of the Jharia and Raniganj specimens the water was more or less clear and colourless In the case of Talchir and Rajmahal specimens the solution was straw coloured The particles of debris were very heavy and numerous and settled very quickly in the test tubes It may be pointed out that, unlike fusain, vitrain goes completely in solution which becomes deep tea coloured When the debris settled some of it was taken out, dried and the fragments were examined and were found to be composed of fibrous strands and angular fragments of different sizes All of them were almost always black and opaque but a few of the fragments and fibres were of a light brown and yellow colour showing some cellular structure Some of these were transparent or semi-transparent and many of the black and opaque splintery fragments showed rows of bordered pits in them

APPEARANCE OF UNTREATED FUSAIN UNDER MICROSCOPE IN TRANSMITTED LIGHT

The powder and fibres were examined under the microscope They were found to be almost black, opaque and sometimes show a scanty cellular structure The cell walls are sometimes seen to be thickened and empty and at other times filled with some colourless to light coloured foreign material showing double refraction The substance appears to be silica Certain thin portions of the fibres and fragments of the fusain were found to be slightly transparent giving rise to a yellowish brown colour They sometimes beautifully preserve layers of bordered pits One or two rows were quite common but three or four rows were also noticed in some cases Mr A K Banerji's work may be mentioned in this connection (*Rec G. S I*, Vol 66, Pt 3)

TREATED COAL MACERATION

With a view to get better results, the fusain specimens were subjected to maceration treatment by a saturated solution of potassium chlorate and concentrated nitric acid (Schulze solution) In some cases with the above treatment the solution was of a pale yellow colour which gave the indication that the coal was highly resistant to the reagent In order to overcome this difficulty, concentrated sulphuric acid was added to the solution which was boiled for some time, thereby making the reacting solution completely efficacious Heating was not carried too far so that the coal itself did not become swollen and charred The fusain specimens were allowed to remain in the solution for a week or two and when the solution was coloured brown the fusain pieces were taken out and washed repeatedly with water in order to get rid of any adhering acids After this treatment the fusain particles were mounted on the slide and were examined under the microscope By the above treatment all the fusain particles did not become transparent or semi-transparent but some of the pieces acquired a slight transparency and could be studied under the microscope The cellular woody structure is not quite common in all the fusain particles But a large number of the Gondwana specimens contained specially thickened cells and tracheids with several vertical rows of bordered pits (uni-seriate, bi-seriate, poly-seriate) One or two rows were quite common whereas three or four rows were found to be present in some of the fragments The pits could be well seen and were of different shape and size In some cases the pits were rounded and circular whereas in other fragments the pits were elliptical and long and narrow and arranged in two rows situated alternately The description of the pits is given below —

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[1] Fuel Bulletin, No 1, pp. 25–27

The xylem is composed of tracheids with bordered pits The pits are round or oval and are arranged on the surface wall in one, two or three vertical rows In some cases two rings of bordered pits and the common wall between adjacent pits are clearly discernible The uni-seriate tracheids are on an average 40μ ($1\mu =$ 001 mm) across and the pits (outer ring) 10μ in diameter (magnification 800 times) The evidence clearly points to the conclusion that it is a gymnospermous wood

It may be mentioned that the Gondwana fusains have a very large number of fragments containing such characteristic bordered pits

When the Salt Range fusain was similarly treated and examined under the microscope it was found that the majority of the fragments remained black and opaque Some of the fragments were however of a semi-transparent and of a yellowish brown colour but did not show much woody structure in them. On the other hand, only a very small number of pieces revealed some structure The few fragments of a yellowish brown colour contained tracheids with uni-seriate bordered pits The cavities were of very small dimension and of rounded nature These pits did not show the characteristic features in the same way as in the case of the Gondwana fusains A few fragments also contain simple pits Several fragments of wood which are more in number than those just mentioned were found to be present in transverse section showing the water-conducting cavities of different sizes arranged in a more or less regular manner Evidently these are not bordered pits The bigger cavities are arranged in one row succeeded by another of much smaller cavities, possibly protoxylem and metaxylem, suggesting a dicotyledon Many pieces of fusain have well-shaped curved boundaries showing that the pieces have broken along the water cavities The intervening spaces however remained absolutely black and opaque under the microscope without showing any woody cellular structure The regular arrangement of the cavities shows that they are fragments of angiospermous wood (dicot) There are also many fragments in which the vessels are scattered in an irregular manner suggesting monocot The microscopic study thus tends to prove that the Salt Range Tertiary (Eocene) coal is composed of very small amounts of gymnospermous and of more profuse angiospermous wood both dicot and monocot The Gondwana fusains under discussion however have been derived from the degradation of a rich gymnospermous flora

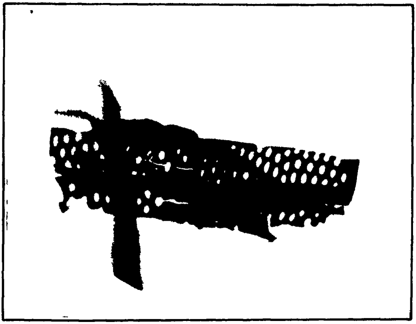

FIG 1 —Talchir Fusain showing bordered pits in tracheids, Transmitted light × 300 (Micro-photo)

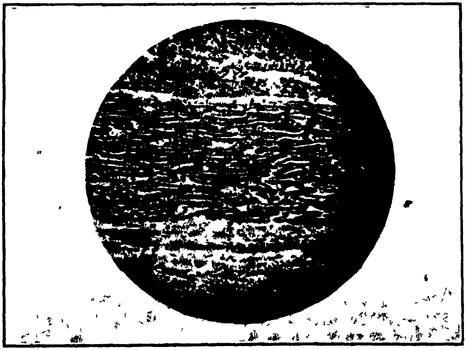

FIG. 2.—Borachak Fusain. × 60. Reflected light (micro-photo).

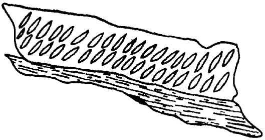

FIG. 3—Camera lucida drawing. Hurra Fusain showing bordered pits × 600

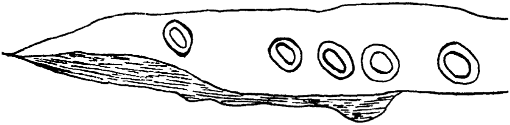

FIG 4—Camera lucida drawing Borachak fusain tracheid showing bordered pits × 800

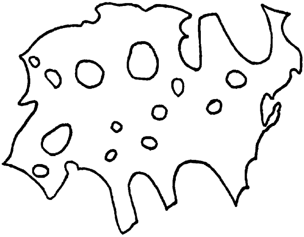

FIG 5—Camera lucida drawing Ara fusain showing vessels × 800

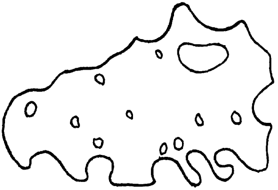

FIG 6—Camera lucida drawing Ara Fusain showing vessels × 800

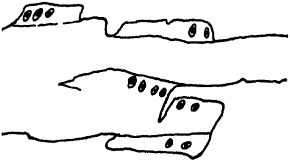

FIG. 7.—Camera lucida drawing Ara Fusain showing tracheids with b. pits. × 600.

MICROSCOPIC DETERMINATION OF THE BARAKAR AND RANIGANJ SANDSTONES OF JHARIA COALFIELD.

By S K ROY, *Ph D* (*Zurich*), *Dhanbad*

The two coal measures of the Jharia coalfield are the Lower Coal Measures, or the Barakar series, and the upper Coal Measures, or the Raniganj series Macroscopically the rocks comprising these two series are similar, the most important difference being that the sandstones of the Barakar series are usually coarser-grained and lighter coloured (more white) than those of the Raniganj series which are also calcareous But sometimes we come across sandstones belonging to these two coal measures which look exactly alike in the hand-specimens as well as in the field And, in case of any such doubt, as to whether the sandstone under question belongs to the Raniganj or Barakar series, the problem can be easily solved by means of its heavy mineral assemblage Fossil evidence is also conclusive, but, as is well known, fossils are not so common, nor are they so easily to be identified as the minerals under the microscope The microscopic examination of the heavy residue can be carried out with any specimen of sandstone, small or big, and it always gives conclusive results

From an examination of the heavy residue slides of about a thousand different specimens of the Barakar and Raniganj sandstones collected from all over the Jharia coalfield, we have obtained the following interesting results.— Though the heavy mineral suites in the Barakar and the Raniganj beds are the same, *viz* garnet, magnetite, ilmenite, zircon, tourmaline, rutile and epidote, their proportions in the two suites are, however, entirely different In the Raniganj beds, garnet may be as much as 50–90% of the heavy residue, whereas in the Barakars it is never more than 50% and is usually only 1 to 3%. On the other hand, the proportion of zircon is only 1% in the Raniganj beds, whereas it is about 15% in the heavy mineral suites of the Barakar beds. These two minerals provide a very ready means of distinguishing the two series of rocks of the Jharia coalfield from one another The study of the heavy mineral assemblages in the Barakar beds adjoining the various coal seams has given further interesting results

On geological and other evidence Dr Fox has divided the Barakar series into four stages It is interesting that the heavy mineral suites of the Barakar rocks of the Jharia coalfield also justify four sub-divisions of the Barakar rock series, very nearly corresponding to Dr Fox's four stages The proportions of tourmaline and zircon provide easy means of distinguishing these four stages from one another The sandstones of the lowest stage of the Barakars, containing coal seams Nos I to IV, are characterised by the presence of a low tourmaline (about 6%) and moderate zircon (about 20%) contents; the second stage, containing coal seams Nos V to XII, is marked by moderate tourmaline

[Published August 22nd, 1940.

(13 to 25%) and rather low (about 13%) zircon contents In the third stage (containing XIII and XIV seams) tourmaline is still less abundant and zircon is abundant In the rocks of the fourth stage, containing seams XV to XVIII, the proportion of tourmaline increases to about 40%, whereas that of zircon falls down to about 2%

It is interesting to note in this connection that most of the rocks of the Parasnath Hill are garnet-bearing. Pyroxene granulites, garnetiferous gneisses and quartzites and calc-silicate rocks, all containing garnet are quite common in the hill This suggests that these rocks might have supplied the material for the Raniganj series The comparative paucity of garnets in the heavy mineral suites of the Barakar series shows that during that period the drainage system must have been different from that in the Raniganj time

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STUDIES IN COAL BY X-RAY DIFFRACTION METHODS

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Introduction

The application of X-rays to the study of the Coal problem dates back to as early as 1912 H Couriot [1] examined by radiographic methods anthracite, coal, coke, peat, lignite, wood and charcoal Similar results were obtained by J Daniel, [2] by the same method and he attempted to correlate the radiographic appearance of the various samples with their composition as ascertained by chemical analysis Garret and Burton, [3] in 1912, in an important communication on the subject, suggested the development of the method for a rapid and simple means of ascertaining the distribution and aggregation of the ash of coal and for the possibility of discriminating between the various forms of ash, leading to increased knowledge of the origin and structure of coal.

Kemp C Norman [4] in a series of interesting studies on similar lines has perfected a technique to determine with a great degree of accuracy the percentage and mode of distribution of ash in coal The specimens were roughly 5″ × 3″ and they were at a distance of one meter from the focal point of the X-ray tube and exposures varying from 20 seconds to 2 minutes were given and the radiographs recorded on the photographic plates From photometric measurements the ash content was calculated in those cases

The systematic study of coal by X-ray diffraction methods, based on the theory of Debye and Scherrer [5] as modified by Raman and Ramanathan [6], was commenced at Calcutta by the author in 1927 and the materials for the study were generously given by Dr (now Sir) L L Fermor and Dr Cyril S Fox The details of the methods of study as well as of the results were published in a series of papers [7] between 1928 and 1935

Experimental

The source of X-rays for the experiment was a Shearer tube of the usual type with water-cooled aluminium cathode and copper target

The window of the X-ray tube consisted of a circular brass slit which was covered with a thin punctureless aluminium foil kept in contact with a card-board and stuck to the tube by sealing wax The cathode rays impinging on the target gave rise to X-rays which emerged out of the tube through the brass slit The X-ray tube was connected to a system of high vacuum backing pumps. An India-rubber pressure-tubing connected the X-ray tube to the low vacuum side, by suitably pinching this tube with a pinch-cock, the leak to the X-ray tube and hence the vacuum inside it could be easily controlled.

VOL. VI—No. 3. [Published August 22nd, 1940.

The high tension current necessary to run the X-ray tube was supplied by an oil-cooled transformer. Alternating current at 160 V was obtained for the primary of the transformer from a rotary convertor. The high tension terminal of the secondary of the transformer was connected to the cathode of the X-ray tube and the lower potential side was connected to the target and earthed. A milliammeter in the secondary circuit recorded the current passing through the X-ray tube. The safety spark gap of the transformer, intended to provide an alternate path of the current in the event of the tube getting hard through very high vacuum, was 8 cms.

The camera consisted of a rectangular wooden box covered with a lead sheath, having a suitable groove for the sliding of a ¼-size plate-holder. The X-ray beam was collimated by passage through a lead tube containing three small holes in series, the first hole being of 0.75 mm. diameter and the last one (nearest to the camera) being 2 mm. This gradation in the size of the holes prevented the diffraction by the metallic edges of the holes from reaching the photographic plate. A metal disc with a central hole served as the container for the substances, and this disc could be conveniently slipped on to a suitable receptacle of the lead cylinder mentioned above, to get the substance in the path of the pencil of X-rays emerging through the system of slits described. A circular lead disc, suitably suspended from the top of the camera by a wire, served to cut off the direct beam and prevented it from falling on the photographic plate. The X-ray diffraction pattern was received on an 'isozenith' photographic plate contained in the plate-holder.

An exposure of from 2 to 8 hours, depending on the nature of the substance, was given with a current of 5 milliamperes in the tube. The angles of diffraction corresponding to the various rings were calculated as follows. The distance d, between the diffracting substance and the photographic plate, was measured. The radius r of the halo (*i.e.* the distance from the centre of the direct spot to the point on the halo where the intensity is maximum) was determined. The angle of diffraction is then given by $\tan\theta = r/d$. The corresponding grating space 'a' could be calculated by using the Bragg formula —

$$a = \frac{\lambda}{2\sin\theta/2} \quad \text{where } \lambda \text{ is the wave-length of the incident X-rays.}$$

To calculate the size of the diffracting particle, the distance between the points on the halo where the intensity fades to half of the maximum was determined. The Laue equation, when suitably modified thus to the different camera model used in the experiment, becomes:

$$\frac{1}{d} = \frac{1.10}{\lambda}\left[\mathrm{B}\cos\frac{\theta}{2} - \frac{1}{\mathrm{B}}\frac{\pi^2 t^2}{4\mathrm{R}^2}\cos^3\frac{\theta}{2}\right],$$

where, t. the thickness of the flake of substance,

R. the distance of the camera from the substance,

d. the linear dimension of the particle as measured perpendicular to the plane of reflection, and

B: the angular width of the halo, less the natural angular width due to the finite aperture of the incident X-ray beam

The values obtained by the above calculations give the sizes of the diffracting particles to the correct order of magnitude

On Banded Bituminous Coals and their Constitution

A typical lump of banded bituminous coal, taken from a coal seam, generally shows four different constituents These used to be described as dull coal, glossy coal, silky coal and mineral charcoal by the coal miners

Marie Stopes [8], in a well-known paper, distinguished them by their characteristic reactions to certain simple chemical treatments and gave the name 'durain' for the dull coal, 'vitrain' for the glossy coal, 'clarain' for the silky coal and 'fusain' for the mineral charcoal

Clarence A Seylor [9] in a note in 'Nature' pointed out a close correspondence between the lithological classification of Stopes and the botanical nomenclature of Thiessen·

Thiessen			*Stopes*
A Anthraxylon (of homogeneous botanical origin from stems or roots)	A_1 Structure absent, obscure or faint	*Vitrain*	Lustre glossy Fracture conchoidal or semi-conchoidal, not laminated.
	A_2 Structure well preserved	*Fusain*	A_2^i dull, friable
B Attritus of heterogeneous botanical origin, general plant debris	B_1 Much anthraxylon present	*Clarain*	A_2^{ii} Lustre silky, minutely laminated
	B_2 Little anthraxylon present		Lustre silky, minutely laminated.
		Durain	Dull compact.

All the above constituents, except clarain, are present in Indian coals, and have been studied by X-ray methods

Let us first consider vitrain It is generally regarded as representing the fundamental coal substance Several investigators,[10] particularly Tideswell and Wheeler, have suggested that its origin is from a jelly-like peat called 'dopplerite' which has lost its water on drying, thus becoming brittle, with a conchoidal fracture and having a shining black appearance

The X-ray evidence is in conformity with the above results. In the first place, vitrain shows two haloes, one intense and corresponding to a spacing of 3·31 Å U, and the other faint and corresponding to a spacing of 2·12 Å.U. Both of these haloes are in the same positions as those of the hexagonal carbon ring in graphite. This result should not of course be taken to imply the presence of free carbon, but only shows that the 'carboneous matter' of vitrain (which may not be free carbon at all, as Cross and Bevan[11] have shown) contains the hexagonal carbon ring having the same structure as in graphite

In the second place, both the haloes are very diffuse, and indeed a calculation of the particle size from the angular width of the haloes shows that the particles are colloidal, having linear dimensions of the order of 10 to 40 Å U Chemical evidence also points to the same conclusion.

Durain, on the other hand, is seen to give 8 haloes Two of them are the same as in vitrain In the position of these two haloes there is seen to be, from a study of the photographic negative, a great deal of overlapping The other rings, which are not overlapping, are all fairly sharp The durain was ignited in a platinum crucible over a Mecker Burner till constancy of weight was attained and the resulting ash was studied by the X-ray methods Three haloes were given with *a* 4 31 Å U , 3 38 Å U , and 2 49 Å U respectively

For purposes of comparative studies, an X-ray pattern for graphite powder was obtained We see that the superposition of the ash and graphite powder haloes on the vitrain pattern reproduces the pattern we have actually obtained for durain

Here it is of interest to refer to some contributions by Fermor,[12] who, from an examination of the composition of Indian coals in relation to their specific gravity and ash content and moisture, has suggested that vitrain is a colloidal system of the gel or emulsoid type and that durain is a colloidal system of the suspensoid type in which the vitrain is surmised to be the dispersion medium in which the mineral matter and free carbon (the end product of vegetable detritus) are suspended The X-ray results just described are in conformity with the above deductions

Fusain is the last variety of coal examined The specimens have a fine fibrous structure, silky in appearance, soft and friable, soiling the fingers when handled The X-ray pattern of fusain disclosed 8 sharp haloes The strong inner haloes indicated localised spots of intensity characteristic of fibre patterns The interspaces are fairly clear The haziness due to the superposition of haloes observed in the case of durain seems to be almost absent here and the edges of the haloes are more or less uniformly well defined The haloes are seen to correspond to spacings due to free carbon and to ash

There are several theories regarding the formation of fusain deduced from evidence afforded by their nature and association with the other types of coals in the field. Some believe it to be due to forest fires and consequent charring prior to the deposition of plant debris. This view does not find support from studies in Indian coalfields[13] The scarcity of water (which acts as a thermostat during the process of coalification) seems to have been responsible for the formation of fusain The mineral matter in fusain gives the haloes ascribable to silica and alumina and one of these haloes is quite sharp—much like a crystal powder pattern This result suggests that though the woody fibre of the plant debris is mainly responsible for fusain (as indicated by the persistence of the fibre structure) some extraneous mineral matter has also got into association with it. Since both moisture and volatile matter are present in fusain (though in a comparatively smaller quantity) the interspaces between the haloes in the pattern are not quite clear

Thus, each of the three constituents of banded bituminous coals from the Indian coalfields gives a unique X-ray pattern in keeping with its well-known structure and composition The vitrain is seen to be the nearest approach to the fundamental coal substance. For this reason, detailed studies were carried on with specimens of vitrain

Light on Proximate Analysis thrown by X-ray Patterns

An examination of the X-ray patterns in relation to the proximate analysis of the coals brings out certain interesting features There is a general scattering in between the haloes, and the degree of intensity of the general scattering as deduced by visual observations is given by indexes varying from 1 to 10 It is found that the intensity of the general scattering in the X-ray pattern shows an intimate relationship to *the sum of moisture content and volatile matter rather than to either of them individually*

From the work of Mack and Hulett,[14] it is now well established that 'moisture content' in coals as determined by proximate analysis has not the same value as that obtained from dehydrating coals with suitable reagents such as phosphoric pentoxide or sulphuric acid, some of the water is in intimate association with the fundamental coal substance and cannot be dislodged by these treatments. Besides, the water as determined in proximate analysis may, to some extent, be derived from thermal action on the chemical complexes So, the 'proximate analysis' does not break the coal uniquely

The correspondence of the general scattering in the X-ray pattern to the sum of 'moisture content' and 'volatile matter', rather than to either of them individually, seems to suggest strongly that these two are associated more intimately than we seem to understand from our present chemical knowledge In this connection, it is interesting to refer to a recent contribution of W T Thom, Jr [15] who, from a study of several hundreds of proximate analysis carried out in the laboratories of the U S Geological Survey, records that a review of the mode of formation and natural history of coal satisfies us that moisture is a normal and natural ingredient among its volatile constituents, and a knowledge of analytical practice shows that the 'moisture' and 'volatile matter' reported are both mixtures of moisture and volatile matter rather than sharply differentiated distillation fractions

A few of the specimens were dehydrated, and later their 'volatile matter' driven out X-ray patterns were obtained from these samples at each of the stages

With the driving away of 'moisture content' the general scattering shows a little clearing up; side by side with this, the width of the diffraction halo increases perceptibly In the pattern for the 'volatile matter-free' coals, precisely the above process seems to have been carried to completion. The

X-ray pattern for this residual product shows wider haloes with very little general scattering between the direct spot and haloes The peak intensities of the haloes are however quite unaltered, suggesting a structural stability of the diffracting particles The widening of the diffraction halo and the diminution of the general scattering with the above treatments suggest a very intimate association of the 'moisture' and 'volatile matter' with a nucleus of stable structure Incidentally the view set forth earlier about the artificial nature of proximate analysis is further supported from those results

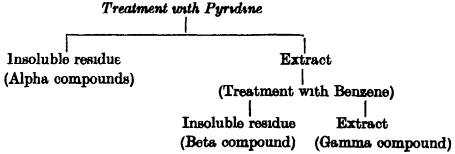
Alpha, Beta, and Gamma Compounds of Coal

In the study of the constitution of coal, organic solvents have been used from very early times We may refer for a comprehensive review of the subject up to 1918 to Stopes' and Wheeler's [16] excellent monograph

In recent years, the extraction of coals by benzene under pressure has been extensively tried by various workers, notably by Bone, Fischer and others

Bedson [17] was the first to show the highly satisfactory results afforded by using pyridine to extract coals Wheeler and his associates [18] in a series of systematic studies broke up coals by pyridine, and the extracted product by benzene or chloroform

Bituminous Coal



They claimed that a nearly complete separation of the coals was effected by the above process into their cellulosic and resinic constituents They attributed similarity of composition to the alpha and beta compounds (cellulosic), whereas the 'gamma compounds' were surmised to be resinic constituents Bone [19] and his students, in a series of detailed investigations with improved technique, have generally agreed with the conclusions drawn by Wheeler and his associates although they pointed out some discrepancies in the inferences of the latter According to Bone [20] the resinic constituents of Wheeler contain not only pure resin, but also some 'humic substance', very probably derived from cellulosic products

The *Alpha*, *Beta* and *Gamma* compounds have also been studied by the author by X-ray diffraction methods Coarsely but not uniformly powdered coal was kept in a suitable thimble and extracted in the absence of air in an all-glass Soxhlet's extraction apparatus An electric heater was used for ensuring uniformity of conditions. The operation was allowed to go on continuously for several days till the pyridine in the chamber showed no coloration even after contact with the coal overnight About 140 hours were usually required for a thorough extraction, resulting in a chocolate brown solution and a black residual product, bereft of any cohesive property Most of the pyridine was recovered by distillation under very low pressure The extract was finally freed from traces of pyridine by keeping in a vacuum desiccator and connecting it to an exhaustion pump The product so obtained was of a madder red colour This was again extracted in the Soxhlet's apparatus with benzene, which took part of it into solution and left behind an insoluble residue All the three products thus obtained were studied by the X-ray methods

From results it is seen that the alpha and beta compounds give nearly identical patterns Their peak intensity is the same, for the beta product there is however a little widening of the haloes (suggesting a finer division of the particles), and a great deal of intense general scattering The gamma compound consists of three haloes, the innermost one is intense and has a somewhat defined edge, the next is diffuse, and the outermost is very faint

The author examined a number of natural and fossil resins from different horizons and ages by X-ray methods[21] with a view to see if the gamma compounds of coal had any structural relationship to those resins, one of the resins thus studied being from the Palana lignites The gamma compound pattern for these resins afford evidence of a more complex composition and structure

In this connection it may be mentioned that the X-ray pattern for the end residual product of Palana peaty lignite, after pressure extraction with 10% NaOH and the subsequent digestion of the residue with 72% sulphuric acid, is much like gamma patterns of coal

The Ash in Coals

The three coals—vitrain, durain and fusain—were heated in a platinum crucible with a Mecker burner for several hours till constancy of weight of the resulting ash was attained The residue in each case was studied by the X-ray methods The ash derived from vitrain shows no distinct intensity maxima, only extremely diffuse haloes are observed. For durain ash there are three maxima, one shows crystal powder spacing, another indicates finer division of the particles and the third is characteristic of centres of diffraction of colloidal dimensions The existence of mineral matter in these three stages is now fairly well established from coal washing methods. It is interesting that Fermor,[22] from the ash-density-relationship, also suggests that some of the ash in the durain is in a colloidal state and part of it may be coarser matter The X-ray results are in conformity with the above observations, from an independent field of research.

For fusain, all the haloes in the ash pattern are more or less well defined and there does not seem to be any colloidal matter in it.

In the coal ash it is now recognised that silica and alumina constitute most of the extraneous mineral matter, though compounds of iron, calcium, etc , may also be present in smaller quantities Calculations of the spacings, for the most important planes of silica and alumina, were made with the help of the well-known equation of Hull It is seen from these results that the ash pattern is primarily due to these two sources of mineral matter, namely silica and alumina

Geological Age and X-ray Pattern

Geologists have long recognised the influence of age and environmental conditions on the process of coalification As the changes however are largely of a structural kind, the chemical researches have not been adequate to bring out conclusively the marked differences between the newer and older coals

It is seen however that the X-ray patterns for the Permo-Carboniferous and Tertiary coals indicate distinct differences Firstly, examining the scattering index of the X-ray pattern in relation to the sum of moisture content and volatile matter, we see that the correspondence is satisfactory only when we divide the coals into two groups—the older and the newer Thus the index gradually rises from 4 to 9, with the rise of the sum of moisture content and volatile matter from 23 9% to 56 62% Coming to the Tertiary group of coals we see that for a smaller percentage of these two ingredients, *i e*, for 46 63% the scattering index is still 9—a result we obtained in the older coals for as large a percentage as 56·62% moisture content + volatile matter The other specimens of the normal Tertiary coals also show such deviation, but the correspondence in the same group of coals between this index and the sum of moisture content and volatile matter is quite satisfactory

Secondly, a more striking difference in the X-ray pattern between the two groups of coals is distinguishable The spacings for the peak intensity of the older group of coals give consistent values of 3·38 Å U for the inner intense halo and 2·12 Å U for the outer faint halo, whereas the corresponding figures for the Tertiary coals are 3·5 Å U and 2 2 Å U respectively The differences noted are beyond the magnitude of experimental errors and are indicative of a fundamental structural difference. This is noteworthy, especially since no definite correlation was possible from other branches of investigation For example, from a study of vitrains of different geological ages, Fermor[23] has recently concluded that no marked correlation is observed between age and any one factor of the proximate analysis but only a minor degree of correlation between age and fuel ratios Examining, however, whether in the same coalfield, the different seams show any orderly change of specific gravity, composition or fuel ratio, he finds that in the Barakar stage, the increasing stratigraphical depth is accompanied by a regular decrease of moisture and volatile matter and an increase of fixed carbon and fuel ratio Similar evidence is adduced from a study of the other coalfields. He suggests that the non-correspondence observed between age and composition in different coalfields may be due to the differences in the original vegetable deposited Since 'proximate analysis' is only an empirically standardised and rather crude artificial process and does not break the coal up into its natural constituents, the observed anomaly is not surprising From a more rational method of disintegrating coal and studying the individual members in detail, Fischer, Broche and Strauch[24] suggest that with increasing geological age of the coals, the ratio of free hydrocarbons to resins increase while the decomposition temperature of the resins are raised

X-ray Study on Tertiary Coals

Chemical and X-ray investigations were carried out with Tertiary coals of the same geological age and horizon, ranging from peaty lignites to anthracites[25] The samples were lignite from Palana in Bikaner State, Rajputana, coals from Mach in Baluchistan and Makarwal in the Salt Range and finally anthracite from Jammu, Kashmir Chemical analyses of the coals indicate that in coalification, the degradation of the cellulose of the vegetable matter is at first rapid, while the lignin is more resistent, in conformity with the generally accepted views, but after a certain stage, the destruction of cellulose seems to proceed at a much lower pace, while that of lignin is more rapid The presence of small amounts of cellulose in coals (as represented by Makarwal and Mach specimens) is an interesting result in this study

Lignins were isolated from the coals by digestion with alkali, and purified The X-ray pattern of all these lignins are practically identical, and resemble the pattern for flax lignin On a comparison of the X-ray patterns for the untreated flax and its lignin, it is seen that except for the observation of fibrous nature in the untreated flax, the haloes in the two cases show great similarity

In the case of lignite from Palana, the end residual products after alkali autoclaving and acid treatment give X-ray patterns very similar to the 'gamma compound' pattern of coals

The X-ray patterns obtained with the peaty lignites and lignitic coals in the untreated state consist of two haloes, one intense, and the other somewhat fainter, the corresponding spacings for the two groups being 3·59 Å U (intense), 2 43 Å U. (faint) and 3·5 Å U (intense) and 2·23 Å U (faint) respectively The anthracitic coal give quite a different pattern showing unmistakable indications of carbon in a fairly coarse state The spacing for the Tertiary coals, *viz* 3·5 Å U are distinctly different from the corresponding values, *viz.* 3 39 Å U. for Permo-Carboniferous coals, in spite of apparent similarity of the composition as determined by 'proximate analysis'. These observations have a relation to the geological history of the coalfields from where the specimens were obtained and a relation to the Bergius theory[26] of coal formation in nature

It is seen that in conformity with the field observations, the X-ray patterns show progressive alteration to the anthracitic stage with increasing pressure.

The Palana lignites which have not been subjected to much pressure show larger spacing for the halo—similar to a pattern for peat, the next set of coals—Mach and Makarwal—have been subjected to moderate pressure and they correspond closely to the normal, Tertiary coals studied from other horizons. The anthracitic coals of Jammu which are from a region of great tectonic activity give patterns characteristic of free carbon and mineral matter.

The distinct difference between the X-ray patterns of the Tertiary and the upper palaeozoic coals, especially the higher spacings for the former in spite of their similar proximate composition, points to a less compact structure of the fundamental coal substance in the Tertiary specimens. The palaeozoic coals seem to have reached the final stage of maturity. In normal palaeozoic strata, anthracitic coals are absent. The existence, however, of anthracites in highly folded regions is attributed to the great pressure to which these regions had been subjected. The results of the X-ray study are in conformity with the above observations and support the Bergius' theory of coal and anthracite formation in nature [26].

Recent studies in the Coal Problem by Workers abroad.

A brief reference may be made to contributions on the X-ray study of coal and associated products by George F Beal and co-workers [27] who have published their results on the study of resins by X-ray diffraction methods and confirm and extend the results obtained by the author from a study of the fossil and natural resins of India. More recently, Von A Boldyrev [28], Director of Federov's institute in Leningrad and his co-worker have made a systematic study of the Russian coals and anthracites, on the lines initiated by the author.

In conclusion it may be mentioned that the systematic study of coal by X-ray diffraction methods opens up vast possibilities both on the academical and industrial side. It is hoped that this subject will attract more workers from all over the world devoted exclusively to this study.

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THE PALAEOBOTANICAL CORRELATION OF COAL SEAMS IN INDIA

By B Sahni, *Sc D*, *F R S*

There is one aspect of 'Coal in India' which I feel has not received due attention in our country and in which considerable progress has been made in recent years in America, England, Belgium, Holland, France, Germany and Russia I mean the correlation of coal seams with the help of the plant remains, particularly the spores, contained in the coal itself

The Polished Section method —I know of only two publications bearing directly upon the subject and these are a brief paper by Dr A K Banerji who investigated in the laboratory of Professor Gothan at Berlin some polished sections of samples of Indian coals (Banerji, A K, Microscopic Study of some Indian Coals *Rec Geol Surv Ind*, LXVI, pp 333–347, 1932-1933), and a brief note by Mr J Lomax published in a paper by G S Caldwell (*Trans. Inst Min. Met*, LXXIV, 1927) This method deserves much further development and no doubt has great possibilities But while polished sections frequently reveal characteristic types of plant remains which can be used for correlation purposes the observations are necessarily limited to the plane of the section

The Maceration method —Much greater possibilities lie in the method by which known quantities of coal, taken from different seams or from exactly measured levels within each seam, can be subjected to maceration in bulk and their 'flora' analysed in detail both quantitatively and qualitatively The variations in the flora from seam to seam or from level to level within a given seam will give the clue to correlations of seams between different coalfields as well as within a coalfield Of course, the limitations of this method should also be admitted: the reliability of the results must depend upon the number and variety of samples investigated

There is urgent need in India of a thorough study, on a large scale, of the spores and cuticles of Indian fossil plants, particularly of those from the Lower Gondwanas, which contain such a vast proportion of our most valuable coals Once we possess a standardised knowledge of the spores and cuticles of known species of plants found in the associated shales, the correlation of these with spores and cuticles obtained by maceration from coal samples would be greatly facilitated with results that may be of far-reaching economic significance.

Luckily, this is a line of investigation that can be pursued by laboratory workers even far removed from the coal areas, provided they are assured of a supply of authentic samples from known localities and horizons.

VOL. VI—No. 3. [Published August 22nd, 1940.

The Geological Survey Department and the coal concerns would do well to provide the relatively small funds necessary for such research before advising or undertaking the expense of large operations that might prove fruitless in the end Incidentally this kind of work provides excellent ground where palaeobotanists working at Universities in India can co-operate with the mining concerns and with the Geological Survey

STATE CONTROL IN THE COAL INDUSTRY[1]

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Introduction

Mining became a major industry in the world about a century ago, at which time every individual (or a group of individuals) in some countries had unrestricted freedom to dispose of his mineral property as he pleased During the past half a century, however, Governments have been gradually encroaching on the rights of the citizen, claiming to act in the public interest An attempt is made in this paper to present a brief review of the extent to which the State interferes in respect of coal mining in some of the important coal producing countries of the world State control has particularly grown since the Great War even in countries which used to be cited as giving complete freedom to private enterprise In other countries where some form of oligarchic or autocratic government exists, the control is so thorough that every industrial enterprise has to fit itself into the national economic structure under the direction of the State

Coal is one of the most important minerals mined in many countries of the world In spite of the phenomenal growth of alternative sources of power like oil, natural gas and hydro-electricity, coal is still the most important of the group as will be seen from the fact that the total output in 1929 amounted to about 1560 million metric tons About 50 countries figure in world statistics as producers of coal, but less than a dozen countries account for nine-tenths of the total world output

U S S R

It is scarcely necessary to say that the coal industry is State-controlled in the Soviet Union The whole industry including mining, processing and distribution is run by the Government according to a well-defined plan We have here large units working to capacity in various parts of the country, and the output is put to the best use possible, with the almost entire elimination of such problems as private profit, waste, over-production, competition, etc. Unlike in many other countries, whatever be the type of coal mined, some use is found for it. The policy of industrialisation pursued by the Government has made the country one of the most important coal producers in the world.

Germany.

Germany ranks as the second largest producer of coal and lignite in the world, whose proved and probable reserves in coal (excluding brown coal)

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VOL. VI—No. 3. [Published August 22nd, 1940.

down to a depth of 2,000 metres have been estimated at over 288,000 million tons Seventy-four per cent of this total is found in the great industrial region of the Ruhr district, and 18 per cent in Upper Silesia

The first effort at control of the coal industry was made in Rhineland in 1893 in order to regulate production and prices A State law in 1919 brought into being district and regional organisations to exercise control over production, prices and distribution of markets, and at the same time to safeguard the interests of workers and consumers The central organisation, the Reichskohlenrat (Coal Council), was virtually dissolved by the Coal Mining Law of 21st April, 1933, and its powers were assumed by the Reichsminister of Economy There are at present several State mines whose aggregate production in 1935 amounted to 17 per cent of the total for Germany All the output from the Saar, about 80 per cent of that from the Hanover region and nearly 9 per cent of that from the Ruhr came from the State mines The ownership of minerals in most parts of Germany is vested in the State, but private ownership still persists in some areas Mining operations are subject to inspection and direction by the Provincial authorities who also enforce laws by which the health and safety of the miners and the safety of the property and public welfare are safeguarded

By 1935, Germany had achieved a considerable degree of rationalisation in order to meet the ever-increasing taxation and other restrictions imposed by the State Between 1924 and 1934 the number of mining units were reduced from 376 to 224, and the number of mines producing over 1 million tons per annum increased from 6 to 26 Extensive mechanisation has resulted in an appreciable increase of output per man-shift during the same period (1670 to 2433 kg per man-shift) Coal is given special preference in freight rates in internal markets and in export by the provision of a sliding scale for long distance transport over rail and water

The brown coal industry of Germany is organised separately from black coal, and controlled by three regional syndicates—the Central Syndicate at Leipzig, the East Elbe at Berlin and the Rhenish at Cologne. These fix the production and sales quotas, prices and sales districts The industry has attained a high pitch of efficiency and much of the brown coal is mined by mechanical scrapers. In the mining districts it is being extensively used for power production and as fuel in a variety of industries and also as domestic fuel in the form of briquettes

Though nominally the industries of Germany are run by private agencies they are very closely controlled and co-ordinated by the Minister of Economy The introduction of the four-year plan and the drive for self-sufficiency have brought about a great improvement in all aspects of the coal industry Better methods of mining, handling and distribution have been evolved. Huge central power stations, run on brown coal, distribute electricity to industrial centres within easy reach. Coke plants and gas plants deliver gaseous fuel through pipe lines to places more than a hundred miles away. Production of motor fuel from coal is now an important industry which was responsible for an output of 55 per cent of the country's requirements of motor fuel in 1936

France

Until the Great War, minerals in France were governed by the Napoleonic laws of 1810, under which concessions were given to lessees in perpetuity with power to transfer the lease as property The law was revised in 1919 and concessions are now granted for 99 years The State is entitled to tax excess profits at rates varying from 10 to 75 per cent, other taxes including the turnover tax are now collected as an *ad valorem* tax amounting to 2 75 per cent of the pit mouth value These latter taxes averaged a total of 9 francs per ton of coal mined in 1934

The State does not conduct any mining operations but has powers of supervision of mines The entire output of France is controlled by about 100 undertakings, 28 of which are responsible for nearly 90 per cent of the national output There are close financial relationships between the coal mines and different industries, *e g* chemical, metallurgical and power supply France produces about 50 million tons of coal per year which meet only two-thirds of her requirements, the rest being imported Several countries participate in this trade, Great Britain leading with about 38 per cent of the import quota, the other chief participants being Germany, Belgium, Netherlands, Poland, U S S R and Indo-china The imports are regulated by licence to different countries under a quota system, and are liable to import duty

There are now regional organisations of producers each with well-defined sales zones and quotas of production and with power to fix prices By the law of 18th August, 1936, the Government has taken powers to regulate prices of domestic and imported coal and to grant subventions to individual organisations which may suffer handicap due to labour laws

Italy

Amongst the Great Powers, Italy has perhaps the least resources in mineral raw materials Good coal occurs only at La Thuile in Piedmont and at Seui in Sardinia, the total output from these being only of the order of 100,000 tons Deposits of lignite occur at Carbonia in Sardinia, Arsa in Istria, and in Tuscany, but the total production is only about 1 8 million tons per annum Italy imports about 12 million tons of coal per annum from Germany, Britain and Poland, the first contributing 60 to 70 per cent of the imports The imports are regulated by the Italian State Railways which act as the controlling and distributing organisation Large sums of money are being spent in exploration and development of the coal resources

Poland.

A national cartel (the Polish Coal Convention) was formed in 1925 amalgamating the three former regional cartels of East Upper Silesia, Cracow and Dombrowa Output and sales quotas are fixed for each mine, both in respect of the home and foreign markets Minimum pithead prices are fixed by the Convention but the Government exercises power over maximum market prices The coals are classified into definite grades and the material is compelled to be marketed under its proper classification

Export is helped by subsidies, the marketing being done by the collieries themselves, subject of course to the regulations laid down by the Convention Poland has now an export agreement with Great Britain in respect of their common markets The original agreement of 1934 was renewed with certain changes in 1937

The State exercises supervision over the National Convention through the Minister for Industries who has powers for controlling output quotas for the internal and export markets and to regulate prices in the home market Export coal is now favoured by specially low freight in order to enable it to compete with British and German coal

Other Central European Countries

In Holland and Czechoslovakia, and particularly in the former, the State mines produce much coal The State mines in Holland also run power plants and coke ovens supplying gas to the public and manufacturing ammonium sulphate which is sold as fertiliser Some of the Czechoslovakia mines are affiliated with the steel, chemical and ceramic industries, but a large number are independent In these and other countries (Belgium, Hungary and Bulgaria) the State exercises control over production and prices

Great Britain

Until very recently the underground mineral rights in Great Britain belonged to the owners of the surface, but these private rights have now been acquired by the Government at a cost of about £65,000,000, the royalty rights thus passing to the State

The first attempt at control was made by legislation in 1930 which empowered the Government to prevent wasteful competition, to control output and to enforce the amalgamation of small and uneconomic properties These powers have since been gradually extended The coal producing areas have been divided into 17 districts in which organisations elected from among the producers have been set up for controlling output and prices Since 1936, each district has a central selling agency. A national organisation regulates the district ones. Export quotas are separate from the internal market quotas. National and regional Investigation Committees have been set up for settling disputes, while the Board of Trade exercises general supervision over the whole scheme.

United States of America

Mineral rights in the Eastern and Mid-western States belong to the surface owners, but in Alaska and some of the Western States they belong to the State

An effort was made under the National Industrial Recovery Act (N R A) of 1933 to establish district organisations for controlling production and prices under the supervision of a Coal Administrator This and the Coal Conservation Act of 1935, in which a small Commission was vested with powers to control prices, were declared unconstitutional by the Supreme Court The Bituminous Coal Act of 1937 became effective in 1937, which aimed at controlling prices It is concerned only with bituminous coal (not with anthracite or other competing fuels) The mines are divided amongst 23 districts, in each of which a controlling Board has been set up The central co-ordinating organisation is the 'National Bituminous Coal Commission' in which there is representation for owners, labour and Government Each district is required, under the provisions of the Act, to submit to the central authority minimum prices for the various grades of coal to be sold within its area, but no provision exists for limiting production or apportioning markets Since non-members (those mines which do not join the district organisations) are penalised by a tax of 19½ per cent on the pit mouth value of the coal produced, the adherence of all mines to the organisation is assured unless they are debarred by the Code which details certain trade practices as unfair

The working of the Act has so far not been successful for it has resulted in an enormous amount of protests and legal actions, so that even early in 1939 the markets were highly disorganised The main provision of the Act to which objection is taken vehemently is the one prohibiting the long established custom of making forward contracts and insisting on fixing prices for only short periods At the same time there is no price control on other competing fuels The coal producers themselves are prohibited from taking concerted action because of the anti-trust laws The Act is, however, still in a state of flux

Canada

The Dominion Government has control over minerals in Yukon and North-west Territories whereas the individual States own the minerals only in the 'Public Lands' under their jurisdiction, *i e* in those areas which were not settled before 1887 The Dominion and State governments have supervision over safety only but have no control over output or prices The Government however helps the industry by giving preferential railway freights so as to equalise competition among the different fields A special bounty is also in force for encouraging the use of Canadian coal in carbonisation plants.

South Africa

The producing fields are mainly in the Transvaal and Natal, the former being responsible for over two-thirds of the total production of the Country.

Natal is however important since it exports half its output There are sales organisations in both the Provinces and quotas are operative for the internal trade and for bunkering, but not for the export trade The export trade is helped by specially cheap railway freights For instance the freight for export coal from the Natal field to the port of Durban (275 miles) is *5s 9d* per ton whereas the freight for the same distance for the internal market is *12s 6d* per ton The export coal is graded and certified as in India, and in fact we seem to have copied South Africa in this respect

Japan

The coal production of Japan is a little less than double that of India There are two organisations, one for the larger producers and the other for the smaller ones, run on a voluntary basis but under Government supervision They fix production quotas and prices The Government has given much encouragement for fuel research, and especially for carbonisation and for the manufacture of motor fuel from coal It is learnt that large plants are under construction for the latter purpose both in Japan and in Manchuria

China

A mining law was promulgated in 1930 by the National Government of Nanking, under which all mineral wealth was declared to belong to the State Prospecting and mining leases were granted by the State, the former for a period of two years and the latter for 20 years but renewable for two further like periods Plans for the introduction of production quotas were under consideration some time before the Japanese invaded the country

India

The coal industry of India, compared to that of many of the countries reviewed above, is relatively free from control Grading has been enforced on export coal since 1926 to enable it to compete with the South African material A cess is levied on soft coke to encourage its marketing but so far no improvements are discernible in the method of its manufacture Arrangements have very recently been made for the establishment of rescue stations in the Jharia and Raniganj fields and compulsory sand-stowing is to be started at a very early date. Except for a certain amount of control on the export coal, there are no measures in force for the control of the industry. There is no price or production control so that the markets are extremely competitive and the private industry is always apprehensive of increased production from the collieries run by the Railways.

General Review.

In most countries efforts have been made in recent years to control output and prices. Endeavour has also been made to encourage export by special freight rates, bounties, etc., and also by concluding agreements with competitors. It should, however, be borne in mind that only 10 per cent of the world's production enters into the international trade, the rest being consumed in the country of origin In maintaining lower prices for export coal, an additional burden is often thrown on the domestic consumer either as higher price or as a form of tax.

A widespread tendency to integration is very evident since the Great War In many countries the smaller and uneconomic properties are compulsorily shut down or amalgamated with other units Thus in the Ruhr district the number of separate undertakings has fallen from 120 in 1893 to 33 in 1936, while the average annual output per colliery has increased six-fold (from half a million tons to three million tons) In Belgium the number of enterprises has been reduced from 122 in 1913 to 86 in 1936, the average production from each mine having risen from 85,000 tons to 160,000 tons In Great Britain the number of separate enterprises has been reduced from 3,289 in 1923 to 2,080 in 1936. In U S A the bituminous coal enterprises numbered 9,331 in 1913 but there were only 6,315 in 1935, while the number of mines producing over 100,000 tons per annum has risen from 70 per cent of the total in 1913 to 80 per cent in 1935

The amalgamation of units engaged in the same industry is called 'horizontal integration' in economic parlance. In 'vertical integration' several different industries are managed by a central organisation, so that all stages of production from the winning of the raw materials to the marketing of the finished product are under unified control Both these types have attained vast dimensions in the Soviet Union and the U S A In Germany also we have examples of both in the coal industry and in the steel and chemical industries Much has been done in Great Britain towards horizontal integration in coal mining We have examples of both types in India in the large business houses which control various industries under the managing agency system. The Japanese controlled South Manchuria Railway in Manchuria and the two or three well-known powerful organisations in Japan are also noteworthy examples. The tendency during the last two or three decades has been towards the building up of similar large organisations in many countries.

In conclusion, I give below a table taken from the 'World Coal Mining Industry' (published by the International Labour Office, Geneva, 1938) in which are summarised the different types of State control, regulation and aid at present in force in several important coal producing countries of the world. The report mentioned above contains much information of value to the coal industry. India can profit to a large extent by the careful study of the experience of other coal producing countries in order to be able to organise her coal industry and make it prosperous.

TABLE 1.—*The economic and commercial set-up of the coal trade and industry in some countries*

Australia	B—Fei—O—P—T—XC
Austria	A—Fet—Q—T
Belgium	A—B—Fei—O—P—Q—TP
Brazil	A—E—H—P—R—TPp
Bulgaria	A—E—Fei—Q—R—T
Canada	A—B—Fi—M—TPp
China	T
Chile	B—C—L—M—R—TP—X
Czechoslovakia	A—Feit—O—P—Q—TP
Denmark	A—E
Finland	A
France	A—Fi—L—O—P—Q—R—TP—X
Germany	A—B—E—Fei—L—O—P—Q—T—X—XC
Great Britain	C—Fe—M—O—P—R—X—XC
Greece	T
Hungary	A—E—Fei—H—P—Q—R—T
India	Fei—R—T.
Fr. Indo-China	T.
Ireland	A—H—Q—Y.
Italy	A—E—H—Q—S—T
Japan	O—Q—T—XC.
Latvia	A—E—H—Qe—T—Y
Mexico	T
New Zealand	H—L—XC
Netherlands	A—Fe—Q—T.
Norway	A
Peru	R—T
Poland	B—C—E—Fei—O—P—Qe—R
Portugal	T
Roumania	A—E—H—Q—TPp
Sweden	A.
Spain	A—E—Fi—H—P—Q—R—TPp.
Switzerland	A—Q—T
Turkey	A—E—H—Qe—R—TPp.
Union of S Africa	Fe—R—T.
U.S.S.R	C—E—O—P—S—Qe.
U.S.A.	M—P—TPp.
Yugoslavia	A—E—H—Q—TPp

Explanation of Symbols

A—Preferential trade agreements and/or special tariff reductions to individual countries.
B—Export bonus, usually from taxes on home production or sales
C—Government guarantees of export credits.
E—Exchange control with permits for foreign exchange to pay for coal imports
F—Special low freight for home mined coal, Fe—to encourage export; Fi—to protect against imports; Ft—to promote transit shipments
H—Preference for home-mined coal in all purchases
L—Government guaranteed loans to rehabilitate mines
M—Shipping subsidies to the merchant marine, usually operating as indirect subsidies for coal exports
O—Schemes for output and sales quotas
P—Control of home market prices
Q—Quotas for imports from different countries, Qe—partial or total embargo
R—Tax rebates or concessions to encourage home production against imports
S—State monopoly of imports
T—Customs duties, TP—protective tariff, TPp—preferential tariff in favour of certain countries
X—Taxes on other fuels so as to encourage coal and discourage other fuels.
XC—Special measures to encourage production of oil from coal
Y—Measures to encourage peat or wood as against coal.

THE ADMINISTRATION OF THE INDIAN MINES ACT, 1923, WHICH CAME INTO FORCE ON THE 1ST JULY, 1924

By W KIRBY, *B Sc , M I Min E , Chief Inspector of Mines in India*

The Indian Mines Act, 1923, applies to British India only

There are 49 sections of this Act, six of which are concerned with the appointment, functions and powers of the Inspectorate Four sections relate to the formation and activities of Mining Boards and Committees, while three sections refer to the duties and responsibilities of owners, agents and managers The health and safety of workers are provided for in six sections of the Act and provision is made for hours of work and limitation of employment The powers of the Central Government to make regulations and of the Provincial Governments to make rules are laid down and penalties and procedure are embodied in the Act

Indian Coal and Metalliferous Mines Regulations were formulated under Section 29 of the Indian Mines Act, 1923, and gazetted in the year 1926 These regulations are prescribed for the safe working of mines and for the submission of the various notices to the District Magistrate and the Chief Inspector of Mines.

Rules for Coal and Metalliferous Mines are made under Section 30 of the Indian Mines Act by the various Provincial Governments These rules provide for:—

Sanitary and Health provisions,
Ambulance, First-Aid and Rescue work,
Registration of work-persons,
Safety of surface,
Abandonment of mines,
Inquiry in the case of accidents,
Certificates of fitness for employment underground of persons who have not completed 17 years of age

Bye-laws for mines

Bye-laws made under section 32 of the Indian Mines Act are framed by the owner, agent or manager of a mine with the approval of the Chief Inspector of Mines or an Inspector for the control and guidance of the persons acting in the management of, or employed in, the mine, to prevent accidents and to provide for the safety, convenience and discipline of the persons employed in the mine.

For the administration of the requirements of the Indian Mines Act the following staff is at present employed.—

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One—Chief Inspector of Mines.
Three—Inspectors of Mines
Four—Junior Inspectors of Mines
One—Electric Inspector of Mines.
One—Assistant Inspector of Mines

For inspection purposes British India is divided into two circles, details of which are given below.—

No 1 Circle

1 All mines in Baluchistan
2 All mines in Bihar except mines in the District of the Santhal Parganas and such mines in the District of Manbhum as lie east of a line drawn from mile 175 on the Bengal Nagpur Railway to mile 169 on the Grant Trunk Road and continued in a straight line across the District.
3 All mines in Orissa
4 All mines in the North-West Frontier Province
5 All mines in the Punjab.
6 All mines in Rajputana
7 All mines in the United Provinces

No 2 Circle.

1 All mines in Assam.
2 All mines in Bengal
3 Such mines in Bihar as lie in the District of the Santhal Parganas and in the District of Manbhum west of a line drawn from mile 175 on the Bengal Nagpur Railway to mile 169 on the Grand Trunk Road and continued in a straight line across the District
4 All mines in Bombay
5 All mines in the Central Provinces
6. All mines in Madras.

Management

Every mine is required to be under the supervision of a manager who has the prescribed qualifications, and who is held responsible for the control, management and direction of the mine, and the owner or agent of every mine is required to appoint himself or some other person having such qualifications to be manager of the mine.

The owner, agent or manager of every mine is responsible that all operations carried on in connection therewith are conducted in accordance with the provisions of the Act and of the regulations, rules and bye-laws and of any orders made thereunder.

The following mines are worked in British India and are regulated by the Indian Mines Act.—

> Coal, iron-ore, manganese ore, gold, chromite ore, copper ore, mica, salt, magnesite, steatite, slate, limestone, stone, sand-stone, fire-clay, china clay, clay, barytes, asbestos, ochre, kaolin, gypsum, beryl, graphite, bauxite, felspar, kyanite and tantalite.

Coal is the principal mineral mined and the output for the year 1937 was 22,335,528 tons of a declared value of Rs 6,98,79,139 The statement below gives the output from the various provinces.—

	Output of coal in tons in 1937.
Assam	243,650
Baluchistan .	19,624
Bengal ..	6,527,820
Bihar	13,835,516
Central Provinces	1,504,159
Orissa .	47,127
Punjab	166,632
TOTAL	22,335,528

During the year 1937, the daily average number of persons working in and about mines regulated by the Indian Mines Act was 267,858 Of these persons, 122,807 worked underground, 72,747 in open workings and 72,304 on the surface Since October 1937 the employment of women has been prohibited underground in mines.

A CONTRIBUTION TO THE EMBRYOLOGY OF THE AMARANTACEAE

By L B KAJALE, *M Sc*, *Department of Botany*, *Benares Hindu University*.

(Communicated by Dr A C Joshi, D Sc)

(*Read August 20, 1940*)

In two earlier papers the writer described the embryology of ***Alternanthera sessilis*** and ***Achyranthes aspera*** (Kajale, 1935 and 1937*a*) In this contribution to the embryology of the Amarantaceae observations have been extended to six more species, representing six other genera of the family, which have not been worked out so far These are ***Celosia argentea*** Linn , ***Allmania nodiflora*** Br , ***Amarantus viridis*** Linn , ***Cyathula tomentosa*** Moq , ***Pupalia lappacea*** Moq. and ***Aerua lanata*** Juss Besides this, the development of the pollen in ***Alternanthera sessilis*** Br , and a few observations on ***Gomphrena globosa*** Linn and ***Bosia Amherstiana*** Hook have also been incorporated in the present report

Schnarf (1931) has summarized the important embryological literature prior to 1931 bearing on the family Amarantaceae This includes the work of Braun, Hofmeister, Fischer, Guignard and Dahlgren Since then embryological investigations on this family have been more extensive An account of seed development in ***Amarantus caudatus*** by Woodcock appeared in 1931 Naithani (1933) published a paper on the microsporogenesis and megasporogenesis of ***Digera arvensis*** This plant has been also investigated by Joshi and Rao (1934) and Puri and Singh (1935) Recently the writer has published two papers The first deals with the female gametophyte of ***Alternanthera sessilis*** (Kajale, 1935), and the second with the life-history of ***Achyranthes aspera*** (Kajale, 1937*a*) Until recently the embryo development in the family, in spite of so much work on the embryo sac, was not known This phase of the life-history has been worked out by Joshi and myself (1937) for ***Alternanthera sessilis*** and ***Digera arvensis*** Souèges (1937) has worked out the development of the embryo in ***Amarantus retroflexus*** and ***A caudatus*** The antipodals of ***Digera arvensis*** and ***Pupalia lappacea*** have been described by Joshi (1936) and the author (Kajale, 1937*b*) respectively As a result of this work, the embryology of three genera of the family ***Digera***, ***Alternanthera*** and ***Achyranthes*** has become fairly known

MATERIAL AND METHODS

The material of ***Celosia argentea***, ***Amarantus viridis***, ***Pupalia lappacea*** and ***Aerua lanata*** is available at Benares and was collected by the author locally.

[Published November 28th, 1940.

It was fixed in Nawaschin's fluid and formalin-acetic-alcohol That of *Cyathula tomentosa* and *Bosia Amherstiana* was fixed in formalin-acetic-alcohol at Mussourie by Dr. A. C Joshi, who kindly placed it at my disposal along with some of the embedded material. The material of *Allmania nodiflora* was sent from Hyderabad (Deccan) by Prof M Sayeeduddin and was also preserved in formalin-acetic-alcohol.

Before sectioning the material, the perianth leaves were removed from the flowers. This is a necessary operation as the perianth leaves in the family are scaly If they are not removed, the material cannot be microtomed smoothly. In order to get good microtome sections of the mature seed, it is desirable that the hard seed-coat should be removed. Its impervious nature does not allow proper infiltration with paraffin and hence smooth microtoming To remove the testa, the seeds were first boiled in water for a few minutes, and then quickly transferred to absolute alcohol, in which they were left for 2 to 5 minutes The testa by this treatment becomes loose and brittle, and can then be removed easily with the help of a pair of needles Sometimes the testa after this treatment breaks off automatically due to sudden dehydration by the absolute alcohol When the testa has been removed, the seeds can be embedded according to the usual methods

Sections for the younger stages were cut 7–9 μ thick and for older stages 10–14 μ thick Heidenhain's iron-alum haematoxylin was chiefly used as a stain, and Tuan's method of de-staining with picric acid was followed.

ORGANOGENY.

The development of the various floral parts has been studied in all plants, and it has been found to be uniform throughout the family. The sequence, in which these parts appear, is bract, bracteoles, perianth, androecium and gynaecium Regarding the details of development reference may be made to Joshi and Rao's (1934) paper on *Digera arvensis* At this place, however, mention may be made about the differentiation of ovules in *Celosia argentea*, as this is different from the rest In other cases the tip of the floral axis after the appearance of all other parts directly transforms itself into the only ovule in the ovary In the multi-ovulate gynaecium of *Celosia*, the floral axis after the differentiation of all other parts gives rise to a number of primordia and each one of them develops separately into an ovule (Figs. 9*a* and 9*b*)

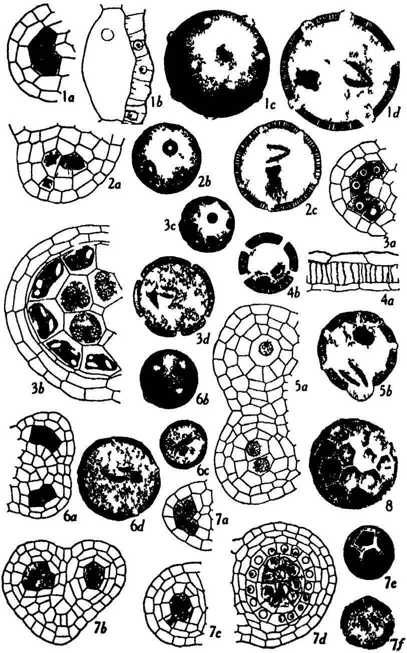
DEVELOPMENT OF ANTHER AND POLLEN.

This phase of the life-history has been studied in all species, and is practically uniform in every case except for some minor differences. The anther to begin with is a mass of uniform cells, but as the archesporium appears it becomes two- or four-lobed. The former condition is found in *Alternanthera sessilis* (Fig. 7*b*), a member of the tribe Gomphreneae (Rendle, 1925), which has one-celled anthers. In the rest of the plants the anthers are four-lobed and ultimately two-celled

The archesporium differentiates either at two or four places, depending upon the one-celled or two-celled condition of the anther at maturity It develops from the hypodermal layer Generally two, three or four vertical rows extending over the entire length of the anther function as archesporial cells (Figs 1*a*, 2*a*, 6*a* and 7*a*) Sometimes the number of rows in *Amarantus viridis* reaches up to five (Fig 3*a*) The writer has also recorded two to four vertical rows of archesporial cells in *Achyranthes aspera* (Kajale, 1937*a*). The condition in *Pupalia lappacea*, however, is different Here the archesporium consists only of a single row of cells (Fig 5*a*) A similar condition has also been reported by Naithani (1933) and Puri and Singh (1935) in *Digera arvensis*

The archesporial cells in each anther-lobe divide periclinally to form two layers, an outer primary parietal layer and an inner primary sporogenous layer (Figs 1*a*, 2*a*, 3*a* and 6*a*) The former now divides periclinally and forms two layers again (Figs 2*a*, 5*a* and 7*b*) The layer on the inner side, resulting from this division, divides once more periclinally (Fig 7*c*) Thus by two successive divisions of the primary parietal layer the wall of the anther, including the epidermis, becomes four layers thick (Figs 3*b* and 7*d*) These layers share a different fate during further development of the anther The layer below the epidermis forms the fibrous endothecium of the mature anther (Figs 1*b* and 4*a*) The thickening bands in the cells of this layer appear when the pollen grains reach the bi-nucleate stage The middle one is crushed at an early stage The innermost layer bordering the sporogenous cells develops in every case into the tapetum (Figs 3*b*, 4*a* and 7*d*) The tapetum is completed on the connective side by the cells adjacent to the sporogenous tissue In function it is of a purely secretory nature No wandering of the tapetal cells to form periplasmodium between the sporocytes was ever observed in any member of the family

The tapetal cells possess a single nucleus in the beginning and are densely packed with cytoplasm During the I meiotic division of the pollen-mother cells the nucleus of the tapetal cells divides mitotically and they become bi-nucleate (Fig 3*b*) A tapetal cell generally does not have more than two nuclei, but occasionally in *Celosia argentea* more than two nuclei were found in some of the cells Up to five nuclei were counted in some cases The nuclei of the tapetal cells in general have one nucleolus in the beginning, but afterwards they have as many as two, three or four nucleoli in them, and sometimes the nuclei may show a lobed appearance (Fig 3*b*) Raghavan (1938) thinks that in *Gynadropsis pentaphylla* such a condition results from the fusion of previously separate nuclei. The writer, however, obtained no evidence for this from his study. In *Cyathula tomentosa* the nucleus of the tapetal cells in many cases has more than one nucleolus from the beginning. This is also seen in other cases, but is rare.



FIGS 1-8

FIG 1 —*Celosia argentea* *a* transverse section of an anther lobe showing the primary sporogenous and primary parietal layers *b* a portion of an anther wall showing granular cutinisation of the fibrous endothecium *c* a pollen grain in surface view *d* mature pollen grain in section showing the 3 nucleate condition and starch grains *a* and *b* ×475 *c* and *d* ×800

FIG 2 —*Allmania nodiflora*. *a* transverse section of an anther lobe showing mitotic divisions of the primary sporogenous cells and periclinal divisions in the primary parietal layer *b* a pollen grain in surface view *c* 3 nucleate mature pollen grain in section *a* ×475 *b* and *c* ×800

FIG 3 —*Amarantus viridis* *a* transverse section of an anther lobe showing three sporogenous cells on the left and two archesporial cells on the right *b* the

same at a later stage showing meiotic divisions in pollen-mother cells. *c*, a pollen grain in surface view *d*, a mature pollen grain in section showing the 3-nucleate condition and starch grains *a* and *b*, ×475, *c* and *d*, ×800.

FIG 4—*Cyathula tomentosa* *a*, a part of the anther wall showing granular cutinization of the tapetum. *b*, a pollen grain in section showing a lenticular generative cell and the tube nucleus *a*, ×475, *b*, ×800.

FIG 5—*Pupalia lappacea*. *a*, transverse section of an anther-half showing sporogenous cells and two parietal layers *b*, a mature pollen grain showing the 3-nucleate condition and starch grains *a*, ×475, *b*, ×800

FIG. 6—*Aerua lanata* *a*, transverse section of an anther-half showing primary parietal and primary sporogenous layers *b*, a pollen grain in surface view. *c*, a mature normal pollen grain in section showing three nuclei and starch grains. *d*, a hypertrophied pollen grain showing the 3-nucleate condition and starch grains *a*, ×475, *b–d*, ×800

FIG 7—*Alternanthera sessilis* *a–d*, transverse sections of anther-lobes showing various stages of development *b* represents a transverse section of a complete anther, while others show only one lobe *e*, a pollen grain in surface view *f*, a mature pollen grain in section showing the 3-nucleate condition and starch grains *a–d*, ×475, *e* and *f*, ×800

FIG 8—*Gomphrena globosa* Pollen grain in surface view ×800

Before the tapetal cells become bi-nucleate they have no vacuoles in them, but afterwards they develop numerous vacuoles and also increase in size (Fig 3*b*) In *Celosia argentea* the tapetal cells are larger than in other cases The tapetum normally persists up to the cytokinesis stage of the pollen-mother cells As the pollen grains develop further it begins to degenerate and disappears completely by the time the pollen grains are mature. In *Cyathula tomentosa* and *Pupalia lappacea* the tapetum shows signs of degeneration rather earlier than in other cases

When the primary parietal layer is undergoing the foregoing changes to form the anther wall, changes also occur in the primary sporogenous tissue. The cells divide mitotically once or twice and differentiate as pollen-mother cells Each of these cells increases in size On the onset of the first meiotic division the protoplasm of the pollen-mother cell retreats from the cell wall and a space is created on all sides in between the protoplasm and its wall (Fig 3*b*) From now onwards the protoplasm gets enveloped in a sheath of mucilage When still enclosed in the sheath, the pollen-mother cells complete the second meiotic division The sheath persists till the cytokinesis is complete and for a short time the four pollen grains remain enclosed in it Afterwards the sheath is disorganized and the pollen grains separate off from each other. By this time the original wall of the mother cell is already disintegrated

During the second meiotic division the nuclear spindles are generally arranged at right angles to each other so as to give rise to a tetrahedral arrangement of the spores (Fig 3*b*), though the isobilateral arrangement is also seen. The four nuclei resulting after the two divisions are connected with each other by the secondary spindle fibres (Fig 3*b*) Thus there are six spindles formed in each of the dividing pollen-mother cells. They gradually disappear·

as cytokinesis begins Cytokinesis takes place by furrowing. The furrows advance from the periphery towards the centre and when they meet they bring about the separation of the four pollen grains

After cytokinesis a curious change takes place in two layers of the anther wall, namely, the tapetum and fibrous endothecium The change consists in the development of small granular markings on the inner side of these layers (Figs 1*b* and 4*a*) These markings first appear on the tapetum (Fig 4*a*) and a little later on the fibrous endothecium (Fig 1*b*) They are generally of microscopical dimensions, and take a somewhat deep stain with haematoxylin Though this is the general condition, they were found to be of a different nature in *Allmania nodiflora* Here the granules are larger than in other plants and appear brownish-yellow in slides stained with haematoxylin

In order to trace the factors that lead to the development of these markings, the material of *Amarantus viridis* was selected for detailed observation Of the two layers, the tapetum is more suitable for this kind of study, since the cells in this layer are larger and more distinct It appears that during cytokinesis or even before that the protoplasm of the tapetal cells retreats from the wall common to the tapetal cells and the adjacent pollen-mother cells This is shown by Fig 3*b* As the microspores are formed, this wall is disorganized and the protoplasm of the tapetal cells on the inner side becomes devoid of any wall Correlated with this, these small granules are deposited on the inner side of the tapetal cells A similar disturbance appears to be caused on the inner side of the anther wall As a result of this, the markings appear on that layer also.

Such markings are recorded by Bhargava (1936) in *Chenopodium album* and re-investigation of *Achyranthes aspera* revealed the presence of the same markings in that plant as well None of the previous authors has recorded them in *Digera arvensis*, but since they occur in all other genera included in the present paper, their presence may be anticipated in that plant also Similar markings have also been seen by the writer on the tapetum of many other plants from different families, now under investigation or previously investigated in this department, such as *Clematis Flammula, Galphimia gracilis, Lilium* sp , *Gisekia pharnaceoides, Boerhaavia diffusa* and *B repanda* It appears, therefore, that they are quite common in the angiosperms Ubisch (1927) and Kosmath (1927) also report the occurrence of such bodies on the tapetum of several angiosperms The latter author has shown that these bodies are of the nature of cutin-like substance

r POLLEN GRAIN.

On the completion of cytokinesis four functional pollen grains result. These very soon become spherical in shape and are enveloped by the intine and exine. The structure of these two layers is described later

The uni-nucleate pollen grain is at first densely filled with cytoplasm From this stage onwards it increases in size, but there is no corresponding increase in the amount of the cytoplasm The nucleus, therefore, with some amount of cytoplasm, comes to be situated on one side, while the other end of the pollen grain becomes vacuolate (Fig *4b*) While still at the periphery, the nucleus undergoes its first division (Fig *4b*) This behaviour of the nucleus to divide at the periphery appears to be a general condition in the angiosperms A few exceptions, where it divides in the middle of the pollen grain, are cited by Wulff and Maheshwari (1938)

The two nuclei, resulting from the first division of the pollen grain nucleus, show considerable difference in size (Fig *4b*) The one larger than the other is the vegetative nucleus, while the smaller one is the generative nucleus The latter is organized into a definite lenticular cell, which is separated by a clear wall from the other (Fig *4b*) This wall in between the two cells is of a very transitory nature and soon disappears, leaving both these nuclei enclosed in the general cytoplasm of the pollen grain Being of very short duration it was clearly seen only in *Allmania nodiflora*, *Amarantus viridis*, *Cyathula tomentosa* and *Pupalia lappacea* Naithani (1933), Joshi and Rao (1934) and Puri and Singh (1935) have reported the organization of a lenticular generative cell in *Digera arvensis* There appears, therefore, no doubt about its presence in other plants of the family

Before the generative nucleus commences its division to form two male gametes, the vacuoles disappear and the pollen grain is completely filled with cytoplasm In this condition the generative nucleus divides into two nuclei and the pollen grain becomes three-nucleate From now onwards the pollen grains take rather a deep stain and are rich in cytoplasm (Figs *1d*, *2c*, *3d*, *5b*, *6c*, *6d*, *7f*) At this stage some starch grains are also deposited in the pollen grains They were found in all cases except in *Allmania nodiflora*, where they could not be clearly observed Similar starch grains have also been recorded by Puri and Singh (1935) in *Digera arvensis* In order to make sure that these pollen grains were not in a state of degeneration I have compared them with those germinating on the stigma I could not trace much difference between these two sets of grains either in their staining capacity or the amount of cytoplasm present in them Puri and Singh (1935) have recorded three-nucleate pollen grains in *Digera arvensis*, but they believe that they were in a state of degeneration My observations do not support their conclusion.

Mention has already been made that the mature pollen grains in the family are three-nucleate (Figs *1d*, *2c*, *3d*, *5b*, *6c*, *6d* and *7f*). Out of the three nuclei, two are sperm nuclei and one is a tube nucleus The sperm nuclei are long spindle-shaped bodies, straight or variously curved They have unevenly distributed chromatin in *Celosia argentea* (Fig. *1d*), *Allmania nodiflora* (Fig *2c*), *Amarantus viridis* and *Aerua lanata* (Figs *6c* and *6d*). In other plants they were very deeply stained and appeared uniformly black in colour. Sperms having unevenly distributed chromatin were previously reported by the writer in *Achyranthes aspera* (Kajale, 1937*a*) Such a structure of the sperm nuclei may be revealed in all cases if they are properly destained. In a few cases, e g *Celosia argentea* and *Amarantus viridis* (Figs 1*d* and 3*d*), the presence of a nucleolus was also observed in the gametes

The tube nucleus is a spherical structure to start with, but during later development it takes a very deep stain and assumes an irregular outline (Figs 1*d*, 2*c*, 3*d*, 5*b*, 6*c*, 6*d* and 7*f*) Further observations on it are described under pollination and fertilisation

The structure of the intine and exine may be described now Out of these two layers the exine is secreted first and soon after that the intine makes its appearance Both the layers differentiate much before the pollen grain nucleus undergoes the first division to form the generative cell The intine is a delicate membrane In the mature grain in some instances it protrudes out slightly through the germ pores along with some protoplasm

The exine is much thicker than the intine In structure it is not uniform As seen in sections, it is composed of light and deep staining parts The latter take the form of radially arranged rods, which are covered on all sides by the light staining portion of the exine (Figs 1*d*, 2*c*, 3*d*, 4*b*, 5*b*, 6*c*, 6*d* and 7*f*) The thickness of the exine and also its tough structure is due to the presence of these rods They are present all round in the exine, except in the region of the germ pores There are some slight differences in their thickness in different species, but these are of too slight a nature to lend themselves easily to description It may be pointed out, however, that in *Allmania nodiflora* and to some extent in *Cyathula tomentosa* and *Celosia argentea* they are thicker than in other species and appear as small dots in surface view (Fig 2*b*) In *Alternanthera sessilis* and *Gomphrena globosa* the rods are more prominent along the ridges of the exine (Figs 7*e* and 8) In the rest of the species they are rather thin and give a fine granular appearance to the surface of the pollen grains (Figs 3*c* and 6*b*)

Sometimes before anthesis a perceptible change takes place in the thickness of the exine. In every case it gets thinner than before, as Puri and Singh (1935) have reported in *Digera arvensis* and previously reported by Brough (1924) in *Styphelia longifolia* The cause for this change according to Brough (1924) is that the material from the exine is drawn upon by the protoplast of the developing pollen grains A somewhat similar opinion has also been expressed by Puri and Singh (1935) They say 'with the increase in size and the approach of the condition, which we regard as leading to degeneration, the exine gets thinner and thinner till it becomes very much reduced in completely degenerated pollen. One can hardly avoid the conclusion that during later stages of development the material composing the exine begins to be dissolved away'. On this point I differ from Puri and Singh (1935), and Brough (1924) The cause of this thinning of the exine in the later stages of pollen development appears to the writer to be its mechanical stretching due to the growth of the protoplast inside it. This can be proved by actual measurement of the distance between the two adjacent deeply staining rods In every case the distance is found to increase.

The exine in *Celosia argentea*, *Allmania nodiflora*, *Amarantus viridis*, *Cyathula tomentosa*, *Pupalia lappacea* and *Aerua lanata* does not bear any spines or ridges on its outside and can be described as 'psilate' according to the terminology of Wodehouse (1935) It is perforated by numerous germ pores, the number of which varies in different species (Figs 1*c*, 2*b*, 3*c* and 6*b*) The pores in *Celosia argentea*, *Allmania nodiflora*, *Pupalia lappacea* and *Aerua lanata* are approximately of the same dimensions, circular and generally equally spaced (Figs 1*c*, 2*b*, 3*c* and 6*b*) To put it in terms of Wodehouse (1935) they are cribilate In *Amarantus viridis* and *Cyathula tomentosa* they are regular or approximately regular A very interesting point about the pores in *Celosia argentea*, *Allmania nodiflora*, *Cyathula tomentosa*, and *Pupalia lappacea* is their arrangement on the exine Each pore, when taken to represent the centre, appears to be regularly surrounded by six or five pores (Figs 1*c*, 2*b* and 3*c*) If the centres of such pores are connected by imaginary lines a figure of a hexagon or pentagon is formed Each pore thus occupies the vertex of a hexagon or pentagon, while one is located in the centre The arrangement repeats itself with regard to any pore The hexagonal arrangement of the pores is more common than the pentagonal arrangement Both the types of pollen grains, however, are found in the same plant or even in the same anther The pore membrane in *Celosia argentea* (Fig 1*c*), *Pupalia lappacea* and *Aerua lanata* (Fig 6*b*) protrudes out of the germ pores, while in the remaining species it does not do so

It should be pointed out here that the psilate type of pollen grains are not found in all members of the family Exception to this type is found in *Alternanthera sessilis* (Fig 7*e*) and *Gomphrena globosa* (Fig 8) The microspores of these plants are distinctly sculptured As both these genera belong to the Gomphreneae it is possible that this may be characteristic of the whole tribe In *Alternanthera* the pollen grains are sculptured with five-sided faces and generally twelve of such faces go to compose the spheroidal body of the pollen grain, which, therefore, has the form of a dodecahedron Occasionally, however, hexagonal faces are also met with in this species. There are as many germ pores as the number of faces, one occupying the centre of each face In *Gomphrena globosa* the faces of the polyhedral grain are generally hexagonal in outline The pentagonal or heptagonal faces may also be found sometimes here and there over the exine in between the hexagonal faces. Normally thirty to thirty-five faces can be counted in a pollen grain, which therefore has the form of a 30–35-sided polyhedron In the centre of each face there is situated a single germ pore

Variation exists with regard to the size of the mature pollen grains in the same species and in different species of the family. Some hypertrophied pollen grains were seen in *Pupalia lappacea*, *Aerua lanata* (Fig. 6*d*) and *Alternanthera sessilis* On closer examination they may be found in other species as well The reasons leading to the development of these grains are not clear, but they might result from irregularities in the reduction division.

The mature pollen grains are spheroidal The following table gives the range of variation in the diameter of the different pollen grains, the number of germ pores, their diameter and the distance between two adjacent pores

From these characters and from the psilate or sculptured nature of the exine it is possible to identify the pollen grains of these plants

PLANT	The diameter of the pollen grain in μ.	The number of germ pores	Diameter of germ pores in μ	The distance between the centres of two adjacent pores in μ
1. *Celosia argentea*	30 to 35	15 to 20	4 to 5 5	8 to 11 5
2 *Allmania nodiflora*	20 to 25	14 to 17	3 5 to 5	7 to 10
3. *Amarantus viridis*	19 to 24	15 to 20	1 5 to 2 2	3 to 5
4. *Cyathula tomentosa*	18 to 24	30 to 35	2 to 3	3 to 4 5
5. *Pupalia lappacea*	20 to 25	20 to 25	2 to 3	5 to 6
6. *Aerua lanata*	14 to 16, and sometimes 20 to 22	6 to 8	3 5 to 4 2	7 to 9
7. *Achyranthes aspera*	15 to 22	25 to 30	2 to 3 5	3 5 to 4 5
8. *Alternanthera sessilis*	16 to 20	12, sometimes more.	2 7 to 3 3	6 to 7
9 *Gomphrena globosa*	25 to 30	30 to 35	2 5 to 3 5	4 5 to 6

THE STRUCTURE OF THE OVARY AND OVULE

The size and shape of the mature ovary vary a good deal in different genera of the family This is shown by figs 9*b*, 11*c*, 12*h*, 13*b*, 14*a* and 15*a* The style is long or short and is capped by a glandular stigma The style is generally hollow, but it is solid in *Amarantus viridis* and *Bosia Amherstiana* (Figs 10*b*, 12*h*)

In *Celosia argentea*, *Amarantus viridis*, *Cyathula tomentosa*, *Pupalia lappacea* and *Aerua lanata* the development and form of the ovule shows little variation. During the early part of its life-history the ovule in all these plants passes more or less through the same stages of development as figured by Joshi and Rao (1934) in *Digera arvensis* (Figs 9*a*, 11*a* and 13*a*), so that at the time of fertilisation it assumes an ana-campylotropus form (Figs. 9*b*, 12*h*, 13*b*, 14*a* and 15*a*) In *Allmania nodiflora*, however, the final form of the ovule is campylotropous (Fig 11*c*) and during its ontogeny it is derived from an amphitropous condition (Fig 11*b*) The development and form of the ovule in *Bosia Amherstiana* is described separately as it differs very much from the rest

Each ovule has a stalk and two integuments enclosing a massive nucellus. The stalk varies in length in different plants It is short in *Amarantus viridis* (Fig 12*h*), while in the remaining plants it is comparatively long (Figs 9*b*, 13*b*, 14*a* and 15*a*) The ovule has two positions with regard to its funicle It is erect in *Celosia argentea* (Fig. 9*b*), *Allmania nodiflora* (Fig. 11*c*) and *Amarantus viridis* (Fig 12*h*) The micropyle in these cases points towards the base of the ovary. In *Cyathula tomentosa* (Fig 13*b*), *Pupalia lappacea* (Fig 14*a*)

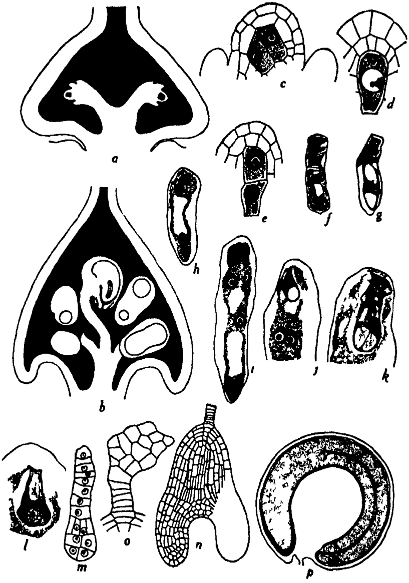


FIG 9.

FIG. 9 —*Celosia argentea* a, longitudinal section of the gynaecium showing two young ovules b, the same at a later stage. c, two megaspore-mother cells. d, a megaspore-mother cell during the I meiotic division. e, a dyad f, a linear tetrad of four megaspores g, a linear row of a micropylar dyad and two megaspores h and i, 4- and 8-nucleate embryo sacs j, micropylar part of an embryo sac showing a synergid and two polar nuclei. k, the same showing a hypertrophied synergid. l, the same showing the egg. m, a stage in the development of the embryo. Dermatogen has just begun to differentiate. n, longitudinal section of an advanced embryo. o, suspensor. p, longitudinal section of the mature seed showing an annular embryo, a single layer of endosperm over the radicle and perisperm. a, × 75, b, × ca 37, c–l, × 475, m and o, × 250, n, × ca.106, p, × ca 18

and *Aerua lanata* (Fig 15a) the ovule has a pendulous position and the micropyle faces towards the stigma The result of this on the course of the pollen tube is described under pollination and fertilization The funicle in *Allmania nodiflora* presents an additional point of interest As the ovule reaches the mature embryo-sac stage, the epidermis of the funicle in its upper part separates off and begins to bulge out This bulging later develops into a hollow arillous outgrowth, which forms a cushion-like structure below the mature seed (Fig 11*c*)

Of the two integuments, the inner one forms the micropyle It is mostly two cells thick, but in the micropylar region it is thicker The outer integument in *Celosia argentea*, *Amarantus viridis* and *Aerua lanata* consists of two layers of cells except in the micropylar part, where it is thicker In *Allmania nodiflora*, *Cyathula tomentosa* and *Pupalia lappacea*, however, the outer integument is thicker both in the chalazal and micropylar region In the chalazal part its thickness varies from three to six or even more layers of cells

The nucellus is quite massive in all cases as in *Digera* (Joshi and Rao, 1934), *Alternanthera* (Kajale, 1935) and *Achyranthes* (Kajale, 1937*a*) It is characterized by the formation of the epidermal cap in all genera, which is generally two to four cells thick The cap formation begins about the time when megaspores are being differentiated (Figs 11*e* and 12*c*) Another feature of the nucellus is the differentiation of a meristematic zone at the chalazal end, which forms new cells and thus helps in the growth of the ovule

During the early part of ovule development a characteristic air-space is developed in the chalazal part of the ovule, in between the two integuments (Figs 10*b*, 11*b*, 12*h* and 13*a*) Sometimes a second air-space may also be seen, e g in *Pupalia lappacea*, near about the first one in between the nucellus and the inner integument The air-spaces may be traced generally up to the fertilization stage (Fig 12*h*) They completely disappear during embryo development The other families of the Centrospermales, in which the presence of an air-space has been recorded, are Chenopodiaceae (Bhargava, 1936), Portulacaceae (Netolitzky, 1926) and Cactaceae (Neumann, 1935). As quoted by Maheshwari (1936) a good deal of importance has been paid by Netolitzky (1926) and Neumann (1935) to the presence of such air-spaces in the ovule from the systematic point of view They appear to be a characteristic feature of the ovule of the Centrospermales In other groups, however, the occurrence of air-spaces between the integuments and the nucellus of the ovule does not appear to be so constant Thus in the Menispermaceae Joshi finds such air-spaces very prominent in *Cocculus villosus* (Joshi, 1937), but they are absent in *Tinospora cordifolia* (Joshi, 1939)

A notable peculiarity has been observed with regard to the structure of the ovule in *Bosia Amherstiana* It has a curved funicle and two integuments, in which is enclosed a very small nucellus (Fig. 10*b*) The nucellus develops up to the appearance of the integumental initials as in other species (Fig 10*a*), but later the growth between the integuments and the nucellus is very unequal. As a result of this the bulk of the ovule, at least up to a certain stage, is mostly composed of integuments alone. The inner one of these forms a long micropyle

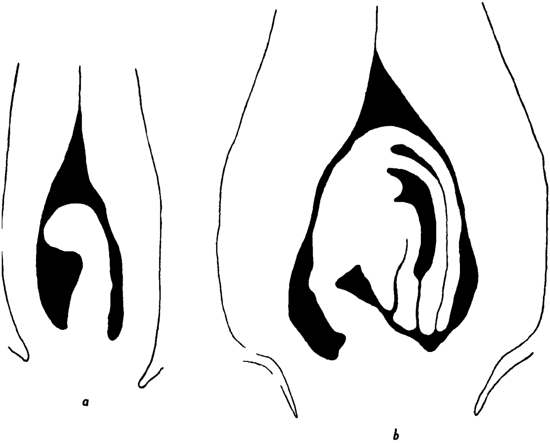


FIG 10

FIG. 10.—*Bosia Amherstiana.* *a* and *b*, longitudinal sections of the ovary showing two stages in the development of the ovule In the latter is seen an air-space in the chalazal part of the ovule and poor development of the nucellus. *a* and *b*, × 125.

and at the base of the latter a very small amount of nucellus is seen (Fig 10*b*). Both the integuments, however, develop side by side The inner one is two cells thick through its greater length, but is thicker in the micropylar part. The outer one is generally two cells thick, but at some places is up to three cells thick. As in many other plants it is thicker in the chalazal and micropylar regions. An air-space is also developed in the chalazal part of the ovule in the early stages. In Amarantaceae it is generally observed that by the time pollen grains become bi-nucleate the functioning megaspore-mother cell is already differentiated, but in the present instance there was no trace of even an archesporial cell at this stage. Older stages than this could not be observed due to lack of suitable material, but it would be really interesting to observe further development of the ovules of this species.

MEGASPORES AND EMBRYO SAC.

The primary archesporium in the ovule begins to appear just before or simultaneously with the differentiation of the integumental initials. It is multicellular and consists of two to six hypodermal cells, except in *Pupalia lappacea*, where mostly only a single cell was observed In addition to the hypodermal archesporium, the cells of the nucellus below the hypodermis also occasionally differentiate as archesporial cells in some plants (Fig 13*c*), as described by Joshi and Venkateswarlu (1935*a*, *b* and 1936) in several Lythraceae

All the archesporial cells, however, do not develop further Those only in the hypodermal position cut off parietal cells In this way two to six megaspore-mother cells may be formed (Figs 9*c*, 11*d*, 12*a*, 13*c* and 15*b*) After having developed to this stage all the megaspore-mother cells merge into the nucellus except the one in the median position, which alone develops further (Figs 9*d*, 11*e*, 12*b*, 13*d* and 15*c*) The fact, that in later stages only one megaspore-mother cell is seen, has probably led older authors to conclude that the archesporium in the family consists of a single cell

The functional megaspore-mother cell increases in size It divides to form two dyad cells (Figs 9*e* and 13*e*) The one resulting on the chalazal side, as a rule in the family, divides into two megaspores (Figs 9*f*, 9*g*, 11*f*, 12*c*, 13*f*, 14*c*, 15*d* and 15*e*) The micropylar dyad cell varies in its behaviour It divides along with the chalazal dyad cell in *Allmania nodiflora* and *Cyathula tomentosa* and thus in these plants generally a regular row of four megaspores is formed (Figs 11*f* and 13*f*), but the division of these two dyad cells is not necessarily simultaneous The micropylar dyad cell shows a tendency to divide rather late (Figs 11*f* and 13*f*) and at times may also fail to divide This tendency for the suppression of the second division in the micropylar dyad cell has become more pronounced in the remaining species, i e *Celosia argentea*, *Amarantus viridis*, *Pupalia lappacea* and *Aerua lanata* In these plants only a row of three cells, two megaspores and a dyad cell, is the usual result of megasporogenesis (Figs 9*g*, 12*c*, 14*c*, 15*d* and 15*e*) Occasionally, however, in *Celosia argentea* both the dyad cells divide and form a row of four megaspores (Fig 9*f*) A row of three cells is reported by Dahlgren (1916) in *Amarantus blitum* and by Fischer (1880) in *Gomphrena decumbens* Out of the eleven plants so far worked out in the family a complete row of four megaspores is present only in *Digera arvensis* (Joshi and Rao, 1934), *Allmania nodiflora* and *Cyathula tomentosa* and even in these a tendency towards the suppression of the second meiotic division in the micropylar dyad is commonly exhibited.

Whatever may be the number of megaspores formed after the two meiotic divisions they are generally arranged in a linear fashion One exceptional case, however, was observed in *Cyathula tomentosa*. This is sketched in fig 13*g* The four megaspores are arranged in an inverted T-shaped fashion. This form of the tetrad has been seen in *Anogra pallida* (Johansen, 1931*b*), *Zauschneria latifolia* (Johansen, 1931*a*) and *Ludwigia parviflora* (Maheshwari and Gupta, 1934) In all these three plants the embryo sac development is of the *Oenothera*-type. In forms with normal-type of embryo sac development such arrangement of megaspores is not known, this being the first recorded instance.

The embryo sac develops always from the chalazal megaspore, while the remaining megaspores degenerate during further development (Figs *9f*, *9g*, *11f*, *14c* and *15e*) The functioning megaspore increases in size Consequently, one or two and sometimes more vacuoles appear on either side of the nucleus (Figs *9g*, *12c*, *13h* and *15d*) The nucleus now divides into two The resulting nuclei show distinct polarity, and they travel to the opposite ends of the embryo sac, being separated by the growing central vacuole (Figs *9f*, *11g*, *12d* and *15g*) Each nucleus at either pole divides twice and this leads to the formation of a typical eight-nucleate embryo sac (Figs *9h*, *9i*, *11h*, *12e*, *13i*, *13j*, *14d* and *15h*)

The egg-apparatus consists of two synergids and an egg cell The latter is a flask-shaped structure with the nucleus confined to the basal part There may be one or two prominent vacuoles in the micropylar part, while below the nucleus a few small vacuoles may also be seen in *Amarantus viridis* (Fig *12g*) and *Pupalia lappacea* (Fig *14f*) In *Cyathula tomentosa* (Fig *13l*) and *Aerua lanata* (Fig *15j*) the egg is very much vacuolate, as already noted in *Achyranthes aspera* (Kajale, 1937*a*)

The synergids are pear-shaped and possess prominent hooks The vacuole is situated in the chalazal end and consequently the nucleus along with some cytoplasm is confined to the upper half (Figs *9j*, *12f*, *13k*, *14f* and *15i*) Occasionally synergids with egg-like appearance, i e with micropylar vacuole and nucleus in the chalazal region are seen in *Amarantus viridis*, *Cyathula tomentosa* and *Pupalia lappacea* Such egg-like synergids now appear to be common in the flowering plants They have been reported from members of several different families, as has been summarized by Joshi and Kajale (1936), and their bearing on the morphology of the synergids has been discussed by Joshi (1939)

The eight nuclei of the embryo sac before they organize into any definite structures are all equal in size, but during the development of the embryo sac the two polar nuclei increase in size as they move to meet each other (Figs *9i*, *9j*, *11h*, *12f* and *13j*) After fusion they form a secondary nucleus This does not occupy any fixed position in the embryo sac It generally lies in the micropylar part and is placed close to the egg-apparatus (Fig *12f*) In *Pupalia lappacea* it is often seen in the chalazal half of the embryo sac, somewhere near the antipodals (Fig *14h*)

The antipodals in the family differentiate before the egg-apparatus. This was clearly observed in *Celosia argentea* (Fig *9i*), and *Allmania nodiflora* (Fig. *11h*). Similar early organization of the antipodals has been recorded by the writer in *Alternanthera sessilis* (1935) In all the members of the family so far investigated the antipodals have been reported to be three in number. The same condition has been observed in *Celosia argentea* (Fig *9i*), *Allmania nodiflora* (Fig *11h*), *Amarantus viridis* (Fig. *12f*), *Cyathula tomentosa*

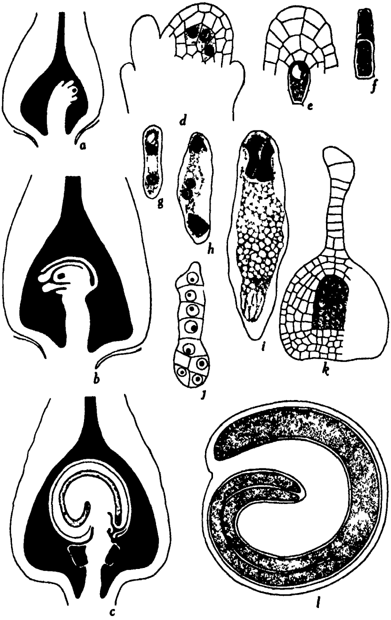


FIG 11

FIG 11.—*Allmania nodiflora* *a–c*, longitudinal sections of the ovary showing three stages in the development of the ovule The last figure shows an arillous outgrowth from the funicle of the ovule *d*, apex of the nucellus showing three megaspore-mother cells. *e*, the same showing a single megaspore-mother cell during the I meiotic division. *f*, a linear tetrad. *g*, 2-nucleate embryo sac *h*, 8-nucleate embryo sac. *i*, embryo sac at an advanced stage showing degenerating synergids. In all the three embryo sacs starch grains are shown by larger dots. *j* and *k*, two stages in the development of the embryo, in the latter figure the dotted part represents the plerome. *l*, longitudinal section of the mature seed showing the form of the embryo and a layer of endosperm over the radicle. *a* and *b*, × 75, *c*, × *ca* 37, *d–j*, × 475; *k*, × *ca*.237, *l*, × *ca* 18.

(Fig 13j) and *Aerua lanata* In *Pupalia lappacea* (Kajale, 1937b), however, the situation is different Here the antipodals are three in the beginning, but they soon begin to multiply All of them divide to form a small mass of cells as shown in figs 14e, g and h Their total number is variable, but up to thirty to forty cells can be commonly counted in the later stages The cells of this antipodal mass are generally small, full of cytoplasm and without vacuoles, but among them a few larger cells are also found and these show prominent vacuoles (Fig 14g) The multiplication of the antipodal cells takes place before the division of the primary endosperm nucleus (Fig 14e). During the secondary elongation of the embryo sac the antipodals are pushed laterally (Figs 14g and h) and there they persist after fertilization up to the early stages of embryo development on one side of the embryo sac as in *Digera arvensis* (Joshi, 1936), *Alternanthera sessilis* (Kajale, 1935) and *Achyranthes aspera* (Kajale, 1937a) The lateral placing of the antipodals after the secondary elongation of the embryo sac has also been clearly observed in *Allmania nodiflora*, *Cyathula tomentosa* and *Aerua lanata*, but in these cases they degenerate earlier than in *Pupalia lappacea* The multiplication of the antipodals in *Pupalia lappacea* recalls the condition found in many members of the Gramineae and Compositae

The occurrence of starch grains in the family has been clearly noted in the embryo sac of *Allmania nodiflora* (Figs 11g, h and i), *Amarantus viridis* (Figs 12f, g and j) and *Cyathula tomentosa* (Figs 13k, l and m) These grains make their appearance in the mature embryo sac or still earlier as in *Allmania nodiflora* (Figs 11g and h) and persist after fertilization for some time in the protoplasm of the endosperm (Fig 12j) In *Amarantus viridis* and *Allmania nodiflora* they are of small dimensions In *Cyathula tomentosa* they are much bigger in size. Their presence appears doubtful in *Pupalia lappacea* and *Aerua lanata*

The final form and size of the embryo sac in the different species is illustrated by figs 11c and 12j A full grown embryo sac in *Celosia argentea*, *Amarantus viridis*, *Cyathula tomentosa* and *Aerua lanata* assumes an annular form In *Allmania nodiflora* and *Pupalia lappacea* it is different In these cases the chalazal end of the embryo sac grows actively and penetrates further into the nucellus (Fig 11c), as in *Achyranthes aspera* (Kajale, 1937a) This development of the embryo sac appears to be correlated with the form of the mature embryo of these plants

POLLINATION AND FERTILIZATION

The flowers in the family Amarantaceae are without honey and odourless. In most cases they appear to be anemophilous In addition to anemophily, self pollination in the family appears in no way rare In those cases where the anthers are nearly as tall as the style or slightly taller, as in *Aerua lanata*, *Alternanthera sessilis*, *Gomphrena globosa*, etc., self pollination appears to be

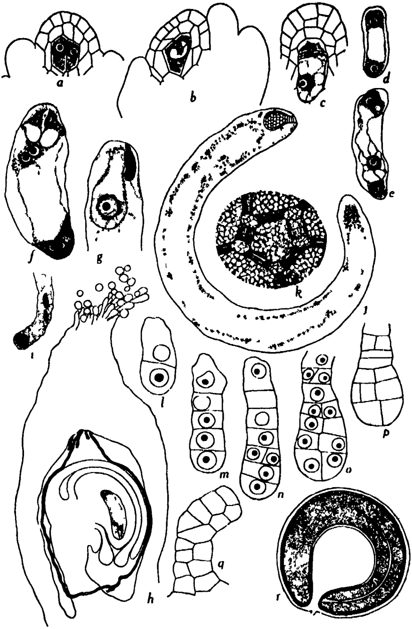


FIG 12

FIG 12.—*Amarantus viridis* *a*, a nucellus showing two megaspore-mother cells *b*, the same showing a single megaspore-mother cell during the I meiotic division. *c*, a linear row of two megaspores and a micropylar dyad Two epidermal cells have divided periclinally *d–f*, different stages in the development of the embryo sac *g*, a micropylar part of the embryo sac showing the fertilized egg and remains of the pollen-tube *h*, longitudinal section of the ovary showing the path and the presence of five pollen-tubes An air space in the chalazal part of the ovule is also seen *i*, apical portion of one of the pollen-tubes from the same ovary. *j*, an embryo sac after fertilization showing mitotic divisions of the endosperm nuclei in the micropylar part and endosperm accumulation at the chalazal end, bigger dots represent starch grains *k*, a portion of the endosperm, cell plates are seen on some spindle fibres *l–p*, various stages in the development of the embryo. *q*, suspensor. *r*, longitudinal section of the mature seed showing annular embryo and a layer of endosperm around it. *a–g*, × 475, *h*, × 125, *i*, × 800, *j*, × *ca*.106, *k*, × 625; *l–q*, × 475; *r*, × 25.

even more common than wind pollination The fact that the stamens are sometimes seen touching the stigma itself lends further support to this possibility Knuth's (1909) account concerning the subject is not exhaustive He has referred to only one plant in the family, viz *Amarantus blitum* He writes that the plants in the Amarantaceae are anemophilous Regarding the Chenopodiaceae, however, he sees the possibility of self pollination This appears to the author to be the case in many members of the Amarantaceae as well

The pollen grain is carried to the stigma at the three-nucleate stage There it germinates and the pollen-tube passes downwards through the style After it has emerged at the lower end of the style, it leaps over the space in between the ovary wall and the ovule It then reaches the ovule and makes its way to the micropyle in either of the two ways This depends upon the form of the ovule at the time of fertilization In *Cyathula tomentosa* (Fig 13*b*), *Pupalia lappacea* (Fig 14*a*) and *Aerua lanata* (Fig 15*a*) the micropyle points upwards towards the stigma In such cases the pollen-tube reaches the micropyle after travelling a short distance along the funicle as described in *Alternanthera sessilis* (Joshi and Kajale, 1937) The orientation of the ovule in *Celosia argentea* (Fig 9*b*), *Allmania nodiflora* (Fig 11*c*) and *Amarantus viridis* (Fig 12*h*) is different The micropyle in these forms is directed in the opposite way, i e , it is pointing towards the base of the ovary Consequently, the pollen-tube, after it has emerged from the style, first comes in contact with that part of the ovule which is facing the stigma It then has to travel along the general surface of the ovule in order to make its way to the micropyle In the latter case, therefore, the pollen-tubes have to undertake a more circuitous path The hanging ovules with their micropyle pointing upwards towards the stigma are better adapted to receive the pollen-tubes

More than one pollen grain has been commonly observed germinating on the stigma As many as five pollen-tubes were seen in *Amarantus viridis* entering the ovary This is illustrated by fig 12*h* Three of the pollen-tubes are seen hanging in the ovary below the style, while the other two have developed so far as to reach the base of the ovary It is not known why these tubes instead of entering the micropyle have gone beyond it to such an extent The ends of these tubes were quite close to one another and in each of them two sperms were clearly seen The tube nucleus is also observed at the tip of one of the pollen-tubes (Fig 12*i*) It becomes evident from fig 12*h* that the path of the pollen-tubes is not very definite after reaching the ovule They run in all directions along the surface of the ovule to find their way to the micropyle

Accessory pollen-tubes entering an embryo sac are quite common in the family They were reported by Joshi and Kajale (1937) in *Alternanthera* and *Digera*, and in *Achyranthes* by Kajale (1937*a*) The writer has now further observed such pollen-tubes in *Pupalia lappacea* and *Aerua lanata*. Among other Centrospermales accessory pollen-tubes have been recorded in the

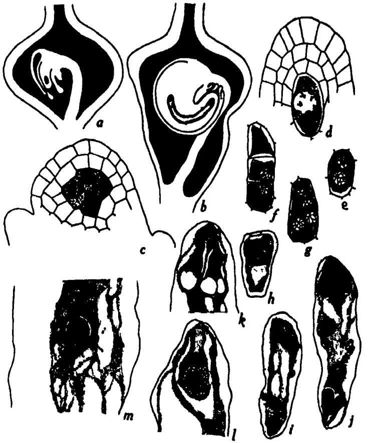


FIG. 13.

FIG 13.—*Cyathula tomentosa* *a* and *b*, longitudinal sections of the ovary showing two stages in the development of the ovule. *c*, apex of a young nucellus showing a group of megaspore-mother cells *d*, megaspore-mother cell at diakenesis *e*, a dyad *f*, a linear tetrad, upper dyad cell is dividing *g*, an inverted T-shaped tetrad *h–j*, various stages in the development of the embryo sac *k*, Micropylar part of the embryo sac showing two synergids and starch grains *l*, the same showing the egg and starch grains *m*, the middle part of the embryo sac showing the primary endosperm nucleus and the starch grains. *a*, × 50, *b*, × 25, *c–m*, × 475.

Nyctaginaceae in *Boerhaavia diffusa* by Maheshwari (1929), and in *B repanda* by the author (1938) Many other cases of a similar nature from different families are known for a long time For full literature on the subject reference may be made to Dahlgren's (1927) review of fertilization

Doubt has often been expressed whether the tube nucleus, which in the later stages of pollen development assumes an irregular outline, can at all take part in the development of the pollen-tube In my opinion this question may be answered in the affirmative In the family Amarantaceae the tube nucleus, though spherical in the beginning, generally becomes irregular in form in mature pollen grains. This was also observed in *Amarantus viridis*. Similarly the tube nucleus in *Gisekia pharnaceoides* becomes irregular in outline (Joshi and Rao, 1936) In both these cases the tube nucleus was clearly seen in the pollen-tubes that had entered the embryo sac (Fig 12*i*) It follows from this that the tube nucleus is likely to take part in the growth of the pollen-tube, and its irregular outline in no way indicates its inert behaviour afterwards

EMBRYO DEVELOPMENT

A fairly exhaustive account of embryo development of *Digera arvensis* and *Alternanthera sessilis* was published by Joshi and the author (1937) recently During the present investigation embryo development has been studied in *Celosia argentea*, *Allmania nodiflora*, *Amarantus viridis*, *Pupalia lappacea* and *Aerua lanata* These observations completely agree with the previous account

After fertilization the oospore by a series of transverse divisions forms a proembryo (Figs 12*l*, 12*m*, 14*i*, 14*j* and 15*k*) It is a filament of varying number of cells Generally it consists of nine to ten cells in *Celosia argentea*, six to eight cells in *Allmania nodiflora* (Fig 11*j*), six to eight in *Amarantus viridis* (Fig 12*n*), eight to ten in *Pupalia lappacea* (Figs 14*j* and *k*) and five to seven in *Aerua lanata* (Fig 15*l*)

Following the organization of the proembryo some of its apical cells, varying from three to five in number (Figs 9*m*, 11*j*, 12*n*, 12*o*, 14*k*, 14*l* and 15*l*), develop further to form the embryo proper It is interesting to note that for a particular plant there is a fixed minimum number of cells which form the mature embryo In *Amarantus viridis* four or five cells take part in the development of the embryo (Figs 12*o* and *p*) Similarly for *Celosia argentea* (Fig 9*m*), *Pupalia lappacea* (Figs 14*k* and *l*) and *Aerua lanata* the minimum number of cells taking part in embryo development is four For *Allmania nodiflora* it is three (Fig 11*j*) To the latter category may be added *Alternanthera sessilis* and *Digera arvensis* (Joshi and Kajale, 1937), where the minimum number of cells that form the embryo is three only

This leads us to the question of differentiation of the various parts of the mature embryo from these apical cells of the proembryo. Only one cell at the extreme apex of the proembryo is concerned in the development of the two cytoledons and the stem-tip Likewise, the root-apex also is developed from a single cell, the hypophysis This may be the third, fourth or fifth cell from the apex, depending upon the initial number of apical cells set apart for building up the mature embryo (Figs. 9*m*, 11*j*, 12*n*, 12*o*, 12*p*, 14*k*, 14*l*, 15*m* and 15*n*) All the cells in between the hypophysis and the apical cell give rise to the hypocotyl and the radicle It is only these parts which develop from a varying number of cells, one, two or three as the case may be.

During further development from the proembryo stage vertical divisions appear in the embryonal cells. These first appear in the second, third or fourth cell from the apex (Fig. 12*n*) In fact this is the division which determines the number of apical cells that are to form the mature embryo The vertical divisions then progress towards the apex, as in Chenopodiaceae

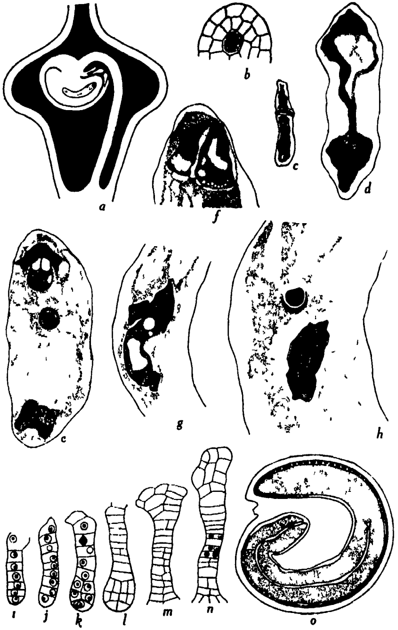


FIG. 14.

FIG 14.—*Pupalia lappacea* *a*, longitudinal section of the ovary showing the form and orientation of the ovule *b*, apex of a young nucellus showing a single megaspore-mother cell *c*, a linear row of two megaspores and a micropylar dyad *d*, an embryo sac showing the 8-free nuclei. *e*, a mature embryo sac showing the egg, two degenerating synergids, secondary nucleus and four antipodals *f*, micropylar part of the embryo sac showing the egg and a synergid *g*, middle part of the embryo sac showing a big vacuolated and four small antipodals *h*, the same showing a mass of antipodals and a primary endosperm nucleus *i*–*l*, various stages in the development of the embryo. *m* and *n*, suspensors *o*, longitudinal section of the mature seed showing the form of the embryo and a layer of endosperm surrounding it on the outside *a*, × *ca* 37, *b*–*h*, × 475, *i*–*n*, × *ca* 237, *o*, × *ca* 18.

(Souèges, 1920), Caryophyllaceae (Souèges, 1924) and Molluginaceae (Joshi and Rao, 1936)

Soon after the completion of the vertical walls in the apical cells, the periclinal divisions are initiated in the same cell in which the first vertical division had started (Figs 9*m* and 12*p*) This is the beginning of the dermatogen differentiation, which is gradually completed in other cells in acropetal order (Figs 14*l* and 15*m*) This acropetal differentiation of the dermatogen appears to be characteristic of the whole order Centrospermales It has been recorded in *Chenopodium Bonus-Henricus* (Souèges, 1920), *Giseka pharnaceoides* (Joshi and Rao, 1936), *Alternanthera sessilis* and *Digera arvensis* (Joshi and Kajale, 1937), *Achyranthes aspera* (Kajale, 1937*a*), *Boerhaavia diffusa* and *B repanda* (Kajale, 1938)

Excluding three to five apical cells, which give rise to the embryo proper, the remaining cells of the proembryo develop into the suspensor This is of two types in the family The first type is found in *Allmania nodiflora* and *Aeura lanata* In both these plants the suspensor throughout its length is uniseriate (Figs 11*k* and 15*m*), as in *Achyranthes aspera* (Kajale, 1937*a*) The second type of suspensor is met with in *Celosia argentea* (Fig 9*o*), *Amarantus viridis* (Fig 12*q*) and *Pupalia lappacea* (Figs 14*m* and *n*) The suspensor in these cases becomes massive in the micropylar region In the lower part, however, it is completely or partially biseriate, as in *Amarantus viridis* (Fig 12*q*) and *Pupalia lappacea* (Figs 14*m* and *n*) or uniseriate as in *Celosia argentea* (Fig 9*o*) A somewhat similar structure is found in *Alternanthera* and *Digera* (Joshi and Kajale, 1937), and Woodcock (1931) has reported the same condition in the species of *Amarantus* worked out by him The suspensor is present nearly up to the stage of embryo development shown by fig 9*n* Later it begins to degenerate and no trace of it is seen in the mature seed

Among the Amarantaceae variation exists with regard to the form of the mature embryo It is annular in *Celosia argentea* (Fig. 9*p*), *Amarantus viridis* (Fig 12*r*), and *Aerua lanata* Examples of annular embryo are found in two more genera, *Alternanthera* and *Digera* (Joshi and Kajale, 1937) The mature embryo in *Allmania nodiflora* and *Pupalia lappacea* is shown by figs 11*l* and 14*o* Here the cotyledons have grown still further into the perisperm as in *Achyranthes aspera* (Kajale, 1937*a*) The structure of the embryo in the last three plants is interesting, for it shows how the spiral embryo, met with in the tribe Spirolobae of the Chenopodiaceae, could have originated

Numerous starch grains are deposited in the different parts of the embryo Their distribution was studied in *Celosia argentea* and *Allmania nodiflora* The cotyledons contain more grains than the hypocotyl and the radicle At the root apex they are less than in any other region The distribution of the starch also differs in the three histogenic layers of the embryo More starch is found in the periblem than in the dermatogen and plerome The size of the grains in the periblem is also larger than in the plerome and dermatogen.

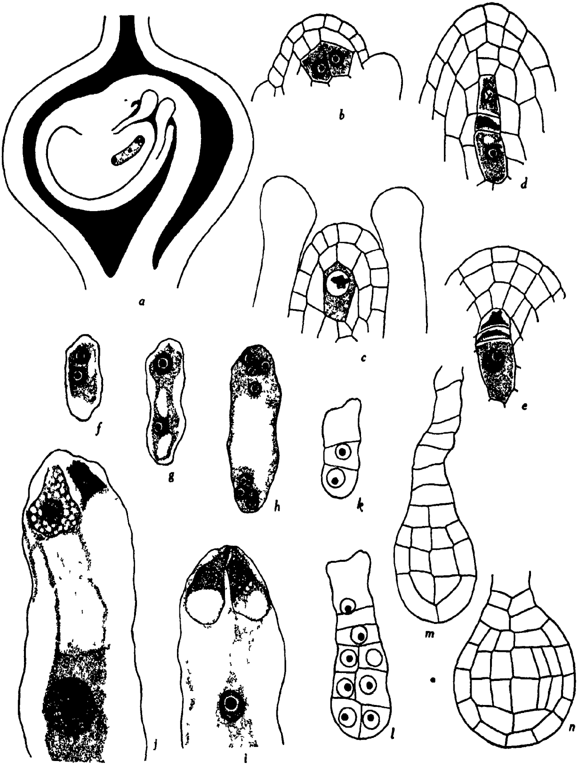


FIG. 15.

FIG. 15.—*Aerua lanata.* *a*, longitudinal section of the ovary showing the form and orientation of the ovule *b*, apex of a young nucellus showing two megaspore-mother cells. *c*, the same showing a single megaspore-mother cell during the I meiotic division. *d* and *e*, a row of two megaspores and a micropylar dyad *f–h*, various stages in the development of the embryo sac *i*, micropylar part of the mature embryo sac showing a pair of synergids and a secondary nucleus *j*, the same showing the fertilized egg and the primary endosperm nucleus. *k–n*, various stages in the development of the embryo. *a*, × *ca.*212; *b–n*, × 950.

The starch deposition in the embryo begins late, after the cotyledons have developed to a considerable size A similar distribution of starch was noted in *Alternanthera* and *Digera* (Joshi and Kajale, 1937)

PERISPERM AND ENDOSPERM

A good deal of nucellus is left in the centre of the mature seed This represents the perisperm The cells in it are densely filled with starch grains, which serve as the reserve food for the embryo The perisperm in *Celosia argentea* (Fig 9*p*) and *Amarantus viridis* (Fig 12*r*) is a pear-shaped body enclosed within the embryo In *Allmania nodiflora* (Fig 11*l*) and *Pupalia lappacea* (Fig 14*o*) it becomes two-lobed due to the accessive growth of the cotyledons

The endosperm formation has been studied in all plants except in *Cyathula tomentosa* The primary endosperm nucleus divides a number of times before the oospore in a free nuclear fashion Numerous nuclei are thus formed These are mostly evenly distributed in the protoplasm of the embryo sac except at the chalazal end In *Celosia argentea*, *Amarantus viridis* (Fig 12*j*), *Pupalia lappacea* and *Aerua lanata* some of the nuclei were clearly seen accumulating in a mass at the chalazal extremity of the embryo sac This accumulation begins after the proembryo stage During later stages of embryo development it disappears due to the appearance of the cell walls in the endosperm

An interesting point about the endosperm is the division of its nuclei All these nuclei do not divide simultaneously throughout the embryo sac. The divisions start in the micropylar region and extend gradually towards the chalazal end The various figures of mitotic divisions thus can be seen in one and the same embryo sac (Fig 12*j*) This peculiar behaviour of the nuclei was clearly noted in *Allmania nodiflora* and *Amarantus viridis* The endosperm nuclei as they enter the telophase stage are connected with each other by spindle fibres (Fig 12*k*) In some of the spindles cell-plates were clearly seen at the equatorial region (Fig 12*k*), but they disappear very soon The spindles also soon disappear and the nuclei lie quite free in the general cytoplasm of the embryo sac

The wall formation in the endosperm begins nearly simultaneously with the appearance of the cotyledonary initials in the embryonal mass It starts in the micropylar region and extends towards the chalazal extremity The endosperm becomes cellular throughout the embryo sac and no endosperm is left in the free nuclear condition To this general rule in the family, *Alternanthera sessilis* (Joshi and Kajale, 1937) is the only exception so far known In this species part of the endosperm at the chalazal extremity remains always in the free nuclear condition and is absorbed by the embryo as such The embryo during its development destroys the endosperm, and the seeds, therefore, are nearly non-endospermic. Only a layer or two of endosperm cells is left in the mature seed This is present in the form of a cap over the radicle in *Celosia argentea* (Fig 9*p*), *Allmania nodiflora* (Fig 11*l*) and *Aerua lanata* In *Amarantus viridis* (Fig 12*r*) and *Pupalia lappacea* (Fig 14*o*) it completely surrounds the embryo except for a short distance about the middle on the side of the perisperm According to Woodcock (1931) the endosperm layer in *Amarantus caudatus* is present only over the radicle, unlike that in *Amarantus viridis* (Fig 12*r*) The cells of the endosperm are generally densely packed with starch grains, but some of these cells in *Pupalia lappacea* (Fig 14*o*) towards the chalazal end have less of starch than others

SUMMARY

The paper deals with the life-history of *Celosia argentea*, *Allmania nodiflora*, *Amarantus viridis*, *Cyathula tomentosa*, *Pupalia lappacea* and *Aerua lanata* A few stages in the development of *Alternanthera sessilis*, *Gomphrena globosa* and *Bosia Amherstiana* are also described

The various floral parts develop in acropetal succession The order of development is bract, bracteoles, perianth, androecium and gynaecium

The archesporium in the anther appears at two places in one-celled anthers and at four places in two-celled anthers and consists of one to five rows of hypodermal cells The primary wall cells give rise to three layers The anther wall is thus four layers thick The hypodermal layer forms the fibrous endothecium The innermost layer develops into the tapetum It is secretory in function Its cells are generally binucleate, but occasionally the number is higher The layer between the endothecium and tapetum is crushed early The inner wall of the tapetal and endothecial cells undergoes granular cutinization in all cases

The division of the pollen-mother cells is simultaneous Cytokinesis takes place by furrowing

The mature pollen grains are three-nucleate The sperms are merely nuclei The tube nucleus becomes irregular in outline, but it appears to take part in the development of the pollen tube The presence of starch grains has been noted in the mature pollen grains The exine in the mature pollen grains becomes thinner than before This is due to its being stretched by growth from inside

The pollen grains in most forms are of the smooth type, but in *Alternanthera* and *Gomphrena* they are sculptured The size of the grains, number and size of the germ pores, behaviour of the pore membrane vary a good deal in the different plants From these characters it is possible to identify the different species of the family

The ovules are generally ana-campylotropous, but in *Allmania nodiflora* the ovule is campylotropous In this species an arillous hollow outgrowth develops from the funicle There are two integuments. The inner one forms the micropyle A characteristic air-space is developed in between the two

integuments in the chalazal part of the ovule A second air-space is sometimes present in between the nucellus and the inner integument

The nucellus is well developed except in *Bosia Amherstiana* Its chief feature is the formation of an epidermal cap and differentiation of a meristematic zone at the chalazal end The archesporium in the ovule consists generally of two to six hypodermal cells, but only of one cell in *Pupalia lappacea* A parietal cell is cut off Many megaspore-mother cells are formed, but only one completes the meiotic divisions A linear row of two megaspores and a dyad or four megaspores is formed The former condition is more common One exceptional case of inverted T-shaped tetrad was noted in *Cyathula tomentosa*

The embryo sac is of the normal type The egg is flask-shaped It may have a single prominent vacuole or many small vacuoles The synergids are two in number, pear-shaped and hooked The vacuole is in the chalazal part and the nucleus is in the micropylar region Egg-like synergids have also been observed The antipodals are three in number, except in *Pupalia,* where they multiply to form a small mass of 30–40 cells They persist for some time The two polar nuclei increase in size before fusion Starch grains in the mature embryo sac have been noted in *Allmania nodiflora, Amarantus viridis* and *Cyathula tomentosa*

Fertilization is porogamous Accessory pollen-tubes in the embryo sac were observed in *Amarantus viridis, Pupalia lappacea* and *Aerua lanata* As many as five pollen-tubes were seen in the ovary of *Amarantus viridis*

The proembryo is a filament of varying number of cells The mature embryo is developed from three to five apical cells of the filamentous proembryo The embryo development corresponds to what has been described in *Alternanthera* and *Digera* (Joshi and Kajale, 1937)

The mature embrye is annular in *Celosia argentea, Amarantus viridis* and *Aerua lanata.* In *Allmania nodiflora* and *Pupalia lappacea* the embryo agrees with that of *Achyranthes.* The suspensor is generally massive at the micropylar end, except in *Allmania nodiflora* and *Aerua lanata,* where it is uniseriate throughout its length

The endosperm is nuclear in the beginning, but later it becomes completely cellular, except in *Alternanthera* In the mature seed the endosperm is left as a layer or two over the radicle An accumulation of the endosperm at the free nuclear stage at the chalazal end of the embryo sac is clearly observed in *Celosia argentea, Amarantus viridis, Pupalia lappacea* and *Aerua lanata*

ACKNOWLEDGMENTS

In conclusion I wish to express my heartfelt thanks to Dr A. C Joshi for his advice and criticism during the investigation My thanks are also due to Prof Sayeeduddin of Osmania University for the material of *Allmania nodiflora*

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THE DETERMINATION OF SOIL CONSTANTS AT BROADCAST AND ULTRA-HIGH FREQUENCIES

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(Communicated by Prof M N Saha, F R S)

(*Read August 20, 1940*)

SUMMARY.

Soil constants have been determined at broadcast and ultra-high frequencies At broadcast frequencies two methods have been employed, viz the Colebrook and Wilmotte method and the differential transformer method The latter has been found to be very simple and quite suitable for the type of work undertaken The variation of soil conductivity, with moisture content, has been studied in both the ranges of frequencies, and it has been found that the conductivity at ultra-high frequency (423 Mc /sec) is about 2 to 8 times (depending upon the moisture content) that at lower frequencies

The conductivity of samples of Allahabad soils at normal moisture contents has been found to be of the order of 2×10^{-13} e m u at broadcast frequencies and $1\ 6 \times 10^{-12}$ e m u at 423 Mc /sec

INTRODUCTION

The knowledge gained of the electrical properties of soil is of considerable importance in physics and electrical engineering, but the development of radio transmission has stimulated great interest in the investigation of these properties at higher frequencies The possibility of predicting ground wave field intensities has rendered such studies indispensable to the radio engineer. It is particularly so in the broadcast range of frequencies where the primary service area can be calculated fairly accurately if the soil constants are known

The mathematical expression for the ground wave field strength was first given by A Sommerfeld [1] According to this the field strength produced by a quarter wave antenna is given by [2]

$$E = \frac{186\ 4\sqrt{P}}{d} A \qquad \ldots \quad \ldots \quad \ldots \quad (1)$$

where E = field strength in millivolts per metre,
P = power radiated in kilowatts,
d = distance from the transmitter in metres,
A = absorption factor and is given approximately by

$$A = \frac{2+\cdot 3p}{2+p+\ 6p^2} \quad . \qquad (2)$$

p is known as the 'Sommerfeld numerical distance' and is given by

$$p = 936\times 10^{-12}\frac{f^2 d}{\sigma} \ . \qquad (3)$$

σ being the conductivity of soil in electromagnetic units and f the carrier frequency in kilocycles per second

Equations (2) and (3) neglect the effect of dielectric constant, as the impedance offered by the soil of good conductivity to the flow of low radio frequency current is primarily resistive The highest frequency at which this is true is given by

$$f = \frac{155\times 10^{15}\sigma}{\kappa} \quad .. \qquad (4)$$

where κ is the dielectric constant of the soil

For ordinary soil the values of σ and κ are of the order of 10^{-13} e m u and 10 respectively, giving f a maximum value of 1,500 Kc./sec , the upper limit of the broadcast range So that, unless the soil is very poorly conducting, the above formulae can be used for the entire broadcast range

For large values of p

$$A = \frac{1}{2\ 08p} \qquad (5)$$

and the distance d at which a field strength E is to be obtained is given by

$$d = \frac{7\ 15}{f}\sqrt{\frac{A\sigma}{E}}\sqrt[4]{P}\times 10^9 \qquad (6)$$

Eqn (6) can be used for determining the primary service area of a broadcast station.

In addition to the above simplified relationships the formulae and curves given by B van der Pol[3] and Dellinger[4] Committees and by Eckersley,[5] Norton[3] and Burrows[6] permit a quick and more accurate computation of the ground wave field strength for all types of soil as well as for sea water.

The soil constants also enter into the calculations of the antenna heights for the greatest fading-free primary range of a broadcast antenna In the case of broadcast transmission fading takes place as a result of the interference of ground wave with the sky wave. The best antenna should, therefore, be of such a height that the sky wave field strength for some desired distance may be small in comparison with that of the ground wave. Ballantine[7] has made a computation by comparing the relative field strengths at various distances for the ground and sky waves radiated from antennas of different heights The ground wave was computed by making use of Sommerfeld's equation and hence involved a knowledge of the ground constants The curves given by him as a result of this analysis can be used to determine the antenna height provided the frequency and ground conductivity are known

Owing to the enormous attenuation of the ground waves and the predominance of sky waves at frequencies above 1,500 Kc /sec the ground constants become only of secondary importance But in the ultra-high frequency range (where the waves are too short to be refracted by the ionosphere, and are propagated by diffraction round the earth's surface) a knowledge of soil conductivity and dielectric constant again becomes essential The formulæ for use at ultra-high frequencies are too complicated to be given here and the curve given by van der Pol,[3] Norton [8] and Burrows [6] can be used for quick and accurate computation

It is important to note that the values of soil constants to be used in the above mentioned curves and formulae are average values for the area under consideration When the variation of soil constants with distance is appreciable this averaging method does not yield very accurate results An attempt to overcome this difficulty was made by Eckersley [9] who gave a method of 'piecing together' attenuation curves corresponding to various soil conductivities But this method though more rational is incapable of yielding more accurate results

The present paper describes laboratory measurements of soil constants in the broadcast range (Part I) as well as at an ultra-high frequency (Part II). The measurements were made with a view to determine these constants for Indian soils and to study their variation with moisture content and frequency. Two samples of soil were tested. Sample I, which was obtained from an open field in the Muir College compound, was studied in 1938-39 and measurements were made both at broadcast and ultra-high frequencies for the same soil The values of conductivity at these frequencies are given in Tables I and IV. Measurements on sample II, obtained from a street about two furlongs from the previous site, were made in 1940, and the values of conductivity for this soil are given in Table II.

MEASUREMENT OF SOIL CONSTANTS AT RADIO FREQUENCY

Soil constants have been studied either by field measurements or by sampling methods in the laboratories For all engineering use the former methods have the advantage of giving average values directly over the specified area, but these methods are always cumbersome and require considerable time for measurements. On the other hand, the sampling methods are quicker and simpler. They have the further advantage that a study of the electrical constants for different types of soils can be employed to predict the constants for other areas from a knowledge of their geological classification and surface conditions. On account of these reasons sampling methods have been recently favoured by various investigators[10]

PART I

The soil constants at the broadcast frequency range were first determined by the balanced differential air transformer method in this laboratory It is a very simple method and has not hitherto been utilized for this purpose by any worker At the same time it has the inherent advantage over the customary Wheatstone bridge method requiring elaborate shielding and stray capacity balancing arrangements A year later measurements of soil constants were also made by the Colebrook and Wilmotte[11] method in the same frequency range

The Differential Transformer Method:—

The construction of the differential transformer and the principle involved is detailed in Hund's 'High Frequency Measurements' (p 268, Ed 1933)

The differential transformer consists of two exactly similar primaries wound in opposite directions and coupled to a secondary When the currents in both the primaries are equal and in the same phase, there is no current in the secondary In order to measure soil constants the condenser containing the sample of soil was connected in one of the arms of the transformer primaries in parallel with another air condenser of about $500\mu\mu F$ capacity The impedance offered by this combination was balanced by another combination of resistance and condenser placed in series with the other arm of the transformer primary The condenser and the resistance were kept in series when the soil was very dry and in parallels when it was wet The soil constants were determined from a knowledge of this resistance and capacitance The current in the secondary was measured by means of a crystal detector and a mirror galvanometer A small parallel plate condenser of about $2\ 6\mu\mu F$ capacity was used as the soil container. The soil was rammed into it and compressed to the extent to which it is normally found in fields

Soil conductivity for sample I was obtained by this method at 1 Mc /sec at different moisture contents and is given in Table I

The Colebrook and Wilmotte Method[11].—

A brief description of this method is given below.—

Two radio frequency oscillators A and B are adjusted to beat at some suitable audible frequency. To one of these, say A, is coupled a LC circuit inductively. Let us designate the capacities of this circuit and of A by C and C_A respectively. If C is varied, the frequency of A changes The original beat frequency is now restored by changing C_A. The variation of C with C_A in this way is illustrated by curves in Fig. 1. Each curve exhibits a maxima (P_1) and a minima (P_2) The values of C corresponding to these

TABLE I

Soil conductivity for Sample I at 1 *Mc /sec*

Percentage of moisture	Conductivity in electro-magnetic units
0·88	$1·1\times10^{-15}$
2·0	$3·9\times10^{-15}$
5·0	$4·0\times10^{-14}$
7·1	$6·3\times10^{-14}$
9·3	$8·3\times10^{-14}$
10·3	$1·1\times10^{-13}$
14·2	$3·0\times10^{-13}$
14·3	$2·2\times10^{-13}$
20·0	$7·9\times10^{-13}$
22·2	$9·4\times10^{-13}$
27·2	$1·0\times10^{-12}$
30·4	$1·06\times10^{-12}$

points determine the resistance of L. If now an impedance, such as is offered by a soil-filled condenser, be connected across C and the curve between C and C_A obtained as before, the points P_1 and P_2 will be found to shift further apart. The value of C corresponding to P_1 and P_2 now will give the total series resistance from which the parallel resistance across C and hence the soil conductivity can be determined. Now if P_1 and P_2 are not sharply defined the corresponding values of C also become relatively inaccurate. It was found that as the soil conductivity of a particular sample increased due to an increase of the moisture content the curve became flatter and flatter (see curves obtained for soil conductivity of 0, 10^{-15} and 10^{-14} e.m.u. in Fig. 1).

Although a tighter coupling between A and the coupled circuit gives sharper peak points, yet the extent to which coupling can be increased is limited by the appearance of an irregular variation followed by the disappearance of the heterodyne beats altogether. Ordinarily the soils have higher conductivity than those for which curves of Fig. 1 have been drawn, so that even the maximum amount of coupling consistent with the regular behaviour of the oscillator does not give sharp points. For this reason the impedance offered by the soil condenser has to be increased by connecting another air condenser in series with it. As soil conductivity increases the value of this capacity has to be decreased so that the points P_1 and P_2 may still be determined within fairly accurate limits.

The order of accuracy to be expected can be estimated from the fact that the difference between the two settings P_1 and P_2 of the coupled circuit capacities could be determined within an uncertainty of about 3–8%. In

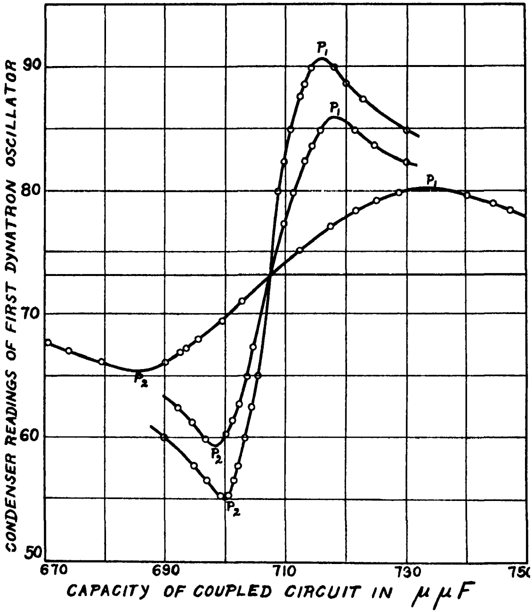

Fig. 1

case the series condenser is not too small the conductivity of the soil may be considered to be proportional to this difference Actual measurements on the same sample of soil with different series capacitance values were found to be consistent well within that limit Measurements on carbon resistances of different values, however, yield results that were within 10% (and in some cases 15%) of their d c. values The results obtained for smaller resistances or for soils of good conductivity (of the order of about 5×10^{-13} e m u) were found to be more inaccurate than those for soils of poorer conductivity. In general an accuracy of about 10% may be assumed in these measurements

Two radio frequency Dynatron oscillators[13] further stabilised by a stage of amplitude control were used in the present investigations A 1,000 cycle tuning fork maintained oscillator was employed as a comparison audio frequency source. A radio receiver was used as a detector of the heterodyne frequency. The sampling condenser, in these measurements, was a cylindrical condenser of 5·7$\mu\mu F$ capacity. Observations were taken at 27°C. in the months of February and March 1940. Results obtained at 1,100 Kc for sample II by this method are given below.—

TABLE II

Soil constants at 1,100 *Kc /sec for Sample II.*

Percentage of moisture	Conductivity in e.m.u.
1·5%	$8{\cdot}6\times10^{-15}$
5·3%	$8{\cdot}0\times10^{-14}$
8·2%	$2{\cdot}0\times10^{-13}$
10·1%	$2{\cdot}9\times10^{-13}$
11·5%	$3{\cdot}0\times10^{-13}$
13·8%	$4{\cdot}7\times10^{-13}$
23·9%	$1{\cdot}1\times10^{-12}$

PART II.

The method employed at higher frequencies was essentially the same as used by Smith-Rose and McPetrie[13] except that a Barkhausen-Kurtz oscillator[14] was employed as a source of high frequency.

The soil container was a wooden box (33·5×16·6×15·5 cm³). The dimensions of the box were so chosen that after filling it completely with soil, practically no change was detected on the wavelength if more soil was heaped over it.

The coupling between the Lecher wire and the oscillating circuit was adjusted according to the moisture content of the soil, so that the wavelength could be easily measured. Tight coupling was found necessary when the moisture content increased beyond 15%.

As detailed in Smith-Rose and McPetrie's paper referred to above the value of

$$y = \left(\frac{\lambda_a}{\lambda_m}\right)^2,$$

(where λ_a is the wavelength measured along the Lecher wire in air and λ_m in the soil) was determined at different moisture contents.

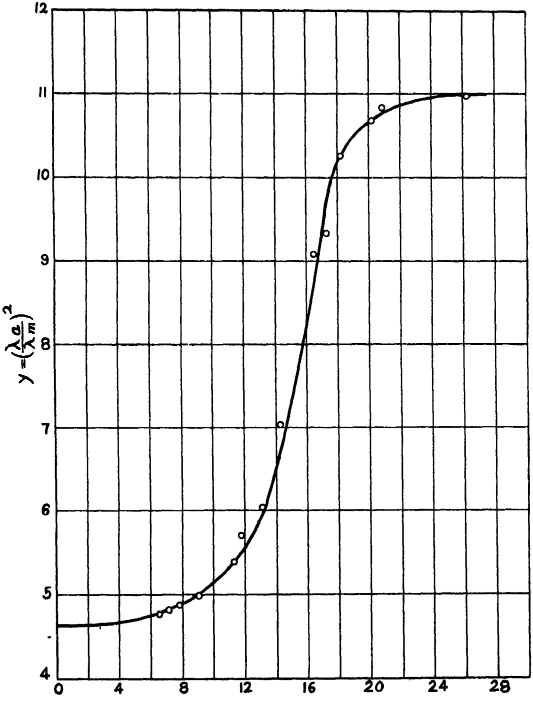

FIG. 2.

A curve was drawn showing the relations between y and the percentage of moisture (Fig 2). The values obtained for y for sample I are given in Table III.

TABLE III

Wavelength in air $\lambda_a = 71$ *cm*

Percentage of moisture	Wavelength in soil in cm	$y = \left(\frac{\lambda_a}{\lambda_m}\right)^2$
6·60	32·60	4·78
7·30	32·30	4·80
7·84	32·28	4·84
9·27	31·80	4·98
11·48	30·70	5·35
11·80	29·74	5·70
13·26	28·66	6·13
14·61	26·80	7·02
16·53	23·50	9·16
17·22	23·32	9·27
18·49	22·18	10·26
20·36	21·74	10·64
21·00	21·58	10·84
26·54	21·44	10·97

From the curve of Fig. 2 it is found that y nearly equals 4·5 for very dry soil and then reaches more or less a constant value 11 for the soil containing moisture above 24 per cent. The quantity y involves both σ and κ, and though the determination of σ and κ individually is not possible we can make certain useful deductions. Measurements detailed in Part I show that the conductivity decreases very rapidly with the moisture content of the soil and therefore we can take the value 4·6 as the value of κ for dry soil, and since κ cannot have a value greater than 11 we conclude that at the frequency corresponding to 71 cm. wavelength (423 Mc./sec.) the dielectric constant must lie between 4·6 and 11 up to 26 percentage of moisture in the soil. The soil was found to contain on the average 17% of moisture at a depth of about 1 foot below the surface in the month of February (1938). All observations were taken at 25°C.

If the percentage of moisture in the soil is known, y can be easily found out from the curve of Fig. 2. From equation (11) of Smith-Rose and McPetrie's paper we have

$$\sigma_{\text{emu.}} = \frac{1}{9\times10^7} f \sqrt{y\,(y-\kappa)} \quad . \quad .. \quad .. \quad (7)$$

The symbols used in equation (7) have the same significance as before. The upper limit of σ is obtained by assuming the least value of $\kappa = 4·6$. The lower limit is obtained by putting $y = \kappa$, for, as will be seen from equation (7), κ cannot be greater than y. The probable value of κ is a suitable value selected between these limits. Table IV below shows some calculations based upon the above methods —

TABLE IV

Conductivity at 423 Mc /sec for Sample I

Moisture content	y	Probable value of κ	Conductivity.	
			For value of κ Col 3	Maximum value of σ for $\kappa = 4\ 6$
6·0	4 75	4 68	$2\ 71 \times 10^{-13}$	$3\ 97 \times 10^{-13}$
9·0	5 0	4 8	$4\ 7 \times 10^{-13}$	$6\ 6 \times 10^{-13}$
11·5	5·5	5 0	$8{\cdot}0 \times 10^{-13}$	$10\ 4 \times 10^{-13}$
15·0	7 4	6 2	$14\ 0 \times 10^{-13}$	$21\ 3 \times 10^{-13}$
17 0	9 5	8 2	$16\ 0 \times 10^{-13}$	$30\ 0 \times 10^{-13}$
18·0	10·1	8 7	$17\ 6 \times 10^{-13}$	$35\ 0 \times 10^{-13}$
20·0	10 6	9·1	$18\ 74 \times 10^{-13}$	$37\ 45 \times 10^{-13}$
24·0	10 9	9 5	$19\ 0 \times 10^{-13}$	$38\ 94 \times 10^{-13}$
28 0	11 0	9·5	$19\ 1 \times 10^{-13}$	$39\ 4 \times 10^{-13}$

DISCUSSION OF RESULTS

The values of conductivity given in Tables I, II and IV are plotted on a logarithmic paper (Fig. 3) Curves I and II give the variation of conductivity with moisture content for samples I and II (Tables I and II) at broadcast frequency. Curve III gives the probable values at the ultra-high frequencies. The dotted curve IV has been plotted for the maximum possible value of conductivities as given in the last column of Table IV

For both the samples of soil the conductivity at the broadcast range was found to increase from about 10^{-15} e m u for very dry soil to 10^{-12} e m u for mud The increase in conductivity was found to be very rapid at lower moisture content, but as the percentage of moisture was increased it was found to fall off, finally approaching a limiting value For normal moisture contents (about 17%) the conductivity of soil approaches its limiting value so that the variation in conductivity for slight seasonal variations in moisture content of the soil is small For the same reason it is not necessary to go on digging the ground (in case it is homogeneous soil) to any great depth and determine its conductivity and moisture content at different levels It is sufficient to dig only a few feet and determine the moisture content till it becomes fairly constant Moreover, it is to be noted that although the variation in moisture content of the surface soil is considerable in certain seasons this variation does not affect the propagation of wireless waves, as a large percentage of the current is usually carried by the soil up to a depth of several metres and the moisture content of the soil at some depth below the surface does not vary to any great extent The normal moisture content in the case of sample I was found to be about 17% in the month of February. The value of conductivity

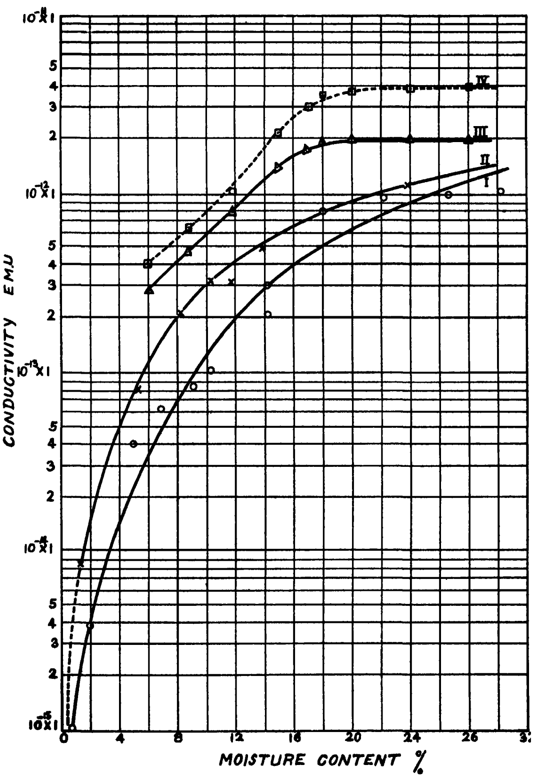

FIG 3.

corresponding to this percentage of moisture (viz. 3×10^{-13} e m u) determines the propagation of ground wave with fair approximation for all seasons and time.

The variation of conductivity with frequency within the broadcast range was not great For this reason only one set of values obtained at about 1 Mc /sec has been given

The values of soil constants for normal moisture content (about 17%) were found to be about 2×10^{-13} at broadcast frequencies

Of the two methods used at the lower frequencies the results obtained by the Colebrook and Wilmotte method is considered to be more accurate for well-known reasons But the differential transformer method is comparatively simple At the same time the latter method appears to be sufficiently accurate A fairly sensitive galvanometer, two good air condensers, a differential transformer and one radio frequency oscillator are the only major requirements of this method On the other hand the Colebrook and Wilmotte method requires two radio frequency oscillators, an audio frequency source, a detector amplifier, and at least three good variable condensers

In addition to this the oscillators to be employed in this case must have very constant frequency, because variations in frequency not only introduce errors in observations but they also make it extremely difficult to take any observations at all This is because zero beat points between the audio oscillator and the heterodyne note has to be obtained and this necessitates very constant frequency source In the case of a differential air transformer method there is of course no difficulty in taking observations even if the frequency varies within narrow limits At the same time appreciable error can be introduced in the results (except at very low moisture content) when the condenser and the resistances in the balancing arm have to be kept in series

It is not too much to expect that the differential transformer method can yield as accurate results as the other one within the limits of accuracy determined by such factors as improper ramming of soil, etc Measurements are being made to compare the results obtained by the two methods for the same sample of soil We are, however, of the opinion, even at this stage, that the differential transformer method is much simpler and sufficiently accurate for all radio propagation determination

The conductivity of soil at high frequencies (423 Mc /sec) was found to increase with moisture content, finally attaining a limiting value of 2×10^{-12} e m u At lower moisture content the value of conductivity was found to be as much as 5 times that at 1 Mc /sec. This difference increased with an increase in the moisture content up to about 17%, the normal moisture content of the soil, when the conductivity was about 8 times as great At still higher moisture content the difference decreased and ultimately became only double of what it was at lower frequencies Smith-Rose [15] had also observed that the conductivity doubled at 100 Mc /sec.

The results obtained by this method are, however, inherently subject to considerable error, but they definitely show that the conductivity at ultra-high frequencies is much greater than that at lower frequencies and, in general, may be considered to be about 3 to 4 times as much or more

Owing to the large amount of soil required for measurement in this case the observations could not be taken at very low moisture content, but from the nature of the curves it appears that the variation at lower moisture content will be less than that in the lower frequency range At higher moisture content the curve becomes flatter than what it is in the case of low frequency range

Smith-Rose and McPetrie had also observed that the conductivity moisture content curve showed a discontinuity at about 14 to 16% moisture, and this they attributed to some sort of resonance phenomenon No such resonance effect was, however, observed in the present investigation

The present work is a preliminary to a more extended investigation in which it is proposed to determine the soil constants at broadcast and ultra-high frequencies at different moisture contents A study of the variation of conductivity with temperature will also be made and representative samples from different localities in India will be tested

Our thanks are due to Prof S Bhargava, the Head of the Physics Department, for the facilities he gave us

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THE NITRATION AND HALOGENATION OF 8, METHOXY- AND 8, HYDROXY-COUMARINS

By B B Dey *and* Miss V Ammalu Kutti

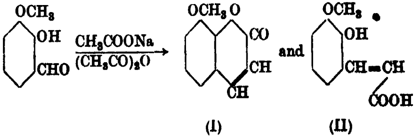
(*Read August 20, 1940*)

The subject of the investigation arose originally in connection with attempts to define precisely the relative positions of the methoxyl groups and the iso-pentane-diol side chain in the molecule of Toddalo-lactone, which had been isolated from *Toddalia Aculeata* and investigated in this laboratory some time ago (Dey and Pillai, *Arch Pharm* , *271*, 1933, 471, and *Arch Pharm* , *273*, 1935, 223, Spath, Dey and Tyray, *Ber* , II, *71*, 1938, pp 1825–1830, and *Ber* , II, *72*, 1939, pp 53–56)

One of the methoxyl groups was supposed to occupy position 8, on account of the rather stable character of the coumarinic acid (*cis*) derived from Toddalo-lactone (Dey and Pillai, *Arch Pharm* , *273*, 1935, 223), and one of the schemes which were drawn up for attacking the problem of its structure was that of the syntheses of several dimethoxy-coumarin-carboxylic acids starting from 8, methoxy-coumarin, and the possible identification of one of these with that resulting from the oxidation of the side chain in Toddalo-lactone.

Although the main purpose with which the investigation was commenced has not been realised, and the underlying idea itself, namely, that one of the methoxyl groups was in position 8, has been shown to be incorrect (Späth, Dey and Tyray, *loc cit.*), the results obtained in the meantime from an investigation of the products of nitration and halogenation of 8, methoxy-coumarin, 8, hydroxy-coumarin and 8, methoxy-coumarin-3, carboxylic acid, which are embodied in this communication have provided materials of considerable interest for a general study of the problem of orientation in the coumarin ring.

8, methoxy-coumarin (Noelting, *Bull Soc Ind Mulhouse*, *79*, 1909, 401–430, Rupp and Linck, *Arch Pharm* , *253*, 1915, 241), required for these investigations, was prepared mainly from ortho-vanillin by the application of Perkin's method, thus —

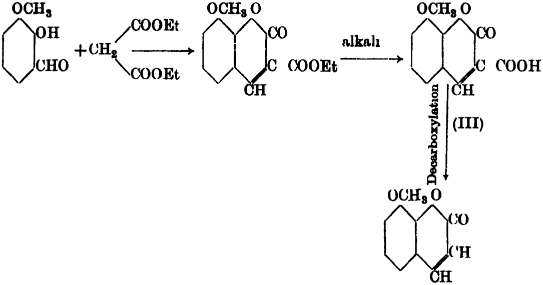


(I) (II)

[Published December 9th, 1940.

Considerable quantities of the corresponding cinnamic acid (II) m p 176°, (methyl ester, m p 106°), were also obtained in this process The formation of this acid, which is always found to accompany the coumarin, does not appear to have been observed either by Noelting or by Rupp and Linck

The acid has apparently the *trans*-formula and cannot be readily converted into the coumarin As the final yield of the coumarin was substantially reduced on account of the formation of this acid, attempts were made to obtain the coumarin by the process of decarboxylation of 8, methoxy-coumarin-3, carboxylic acid (III) which could be prepared in a quantitative yield from the condensation of ortho-vanillin with ethyl malonate in the presence of piperidine (Perkin and Robinson, *J C S*, 1914, 2382), thus —

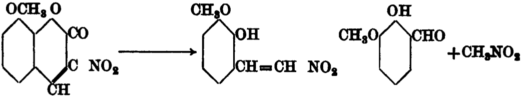


The decarboxylation, which was carried out with copper powder and sand, proceeded, however, with partial decomposition thus diminishing the final yield of the coumarin to about the same as that obtained by the other process

The nitration of 8, methoxy-coumarin was carried out under different conditions Low temperature usually gave an impure product, the mono-nitro-product, (IV), m p 206°, being obtained almost exclusively on treating the coumarin with a mixture of concentrated sulphuric acid and fuming nitric acid at a temperature of 30°–40°

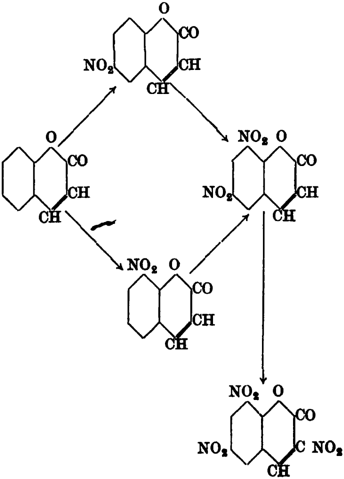
The determination of the position of the nitro-group in this new compound presented an interesting problem, in the solution of which several unforeseen difficulties were encountered.

That the nitro-group had not entered the pyrone ring was proved by the behaviour of the compound with boiling alkali, a *cis*-nitro-cinnamic acid readily changing into the original compound being formed. 3, nitro-coumarins are known to be readily broken down in this reaction, first into nitro-styrene derivatives and then into salicyl-aldehydes, thus:—



The nitration of coumarin itself had been known to proceed in the first place with the exclusive substitution of position-6 (cf Delande, *Annalen*, *45*, 1848, 337, Bleibtreu, *Annalen*, *95*, 1855, 252; Tage, *Ber*, *20*, 1887, 2110; Morgan, *J C S*, *85*, 1904, 1233; Francis, *Ber*, *39*, 1906, 3803), but careful repetition of the work revealed the formation also of small amounts of 8, nitro-coumarin in the process (Dey and Krishnamurthi, *J I C S*, 1927, 1977)

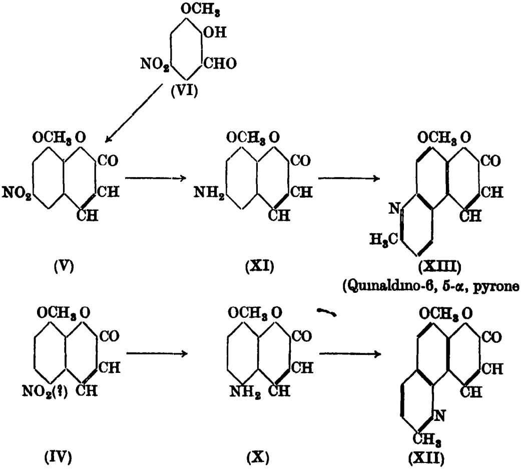
On further nitration, the 6, 8, dinitro- and finally the 3, 6, 8, trinitro-coumarins are formed (cf. Clayton, *J C S*, 1910, 1397), thus.—



If nitration had proceeded similarly to that in the unsubstituted coumarin, the new derivative should be considered to be 6, nitro-8, methoxy-coumarin (V). The synthesis of 6, nitro-8, methoxy-coumarin was readily accomplished, starting from 5, nitro-ortho-vanillin (VI), the position of the nitro-group in the latter having been definitely established by Davies (*J.C.S.*, 1923, 1578).

6, nitro-8, methoxy-coumarin (V) melted at 205° which was very nearly the same as the melting point of IV, but since a mixture of the two melted indefinitely between 170–90°, they were presumed to be different. This presumption was shown to be correct by reducing IV and V to the corresponding amines, X and XI, and preparing therefrom, by diazo-transformations, various derivatives which were all found to be different.

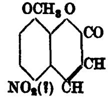
Moreover, two distinct quinaldino-pyrones, XII and XIII, were prepared from the two isomeric amino-8, methoxy-coumarins, X and XI, by the process of Doebner and Miller, thus:—



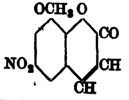
(Quinaldino-6, 5-α, pyrone.)

(Quinaldino-7, 8-α, pyrone.)

The following table containing a statement of the melting points of the various derivatives of the two isomeric nitro-coumarins brings out their differences very clearly:—



(By nitration of 8, methoxy-coumarin.)

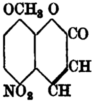


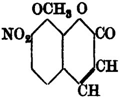
(By Perkin's Syntheses from 5, nitro-ortho-vanillin.)

By Nitration of 8, methoxy-coumarin		By Perkin's Syntheses from 5, nitro-ortho-vanillin		
COMPOUND	M P.	COMPOUND	M P.	MIXED M P.
(?) Nitro-8, methoxy-coumarin	206°	6, nitro-8, methoxy coumarin	205°	170–180°
,, Amino-8, methoxy-coumarin	166°	6, amino 8, methoxy-coumarin	167°	130–148°
,, Acetyl-amino-8, methoxy coumarin	265°	6, acetyl amino, 8, methoxy-coumarin	241°	215–245°
,, Picrate	180°	Picrate	228°	168–200°
,, Chloro-8, methoxy-coumarin	182°	6, chloro-8, methoxy coumarin	122°	120–180°
,, Bromo-8, methoxy-coumarin	168°	6, bromo-8, methoxy-coumarin	110°	105–150°
,, Quinaldino pyrone	217°	Quinaldino pyrone	247°	175–200°

The foregoing observations definitely established the fact that the nitro-group had entered a position other than 6. The methoxyl group in 8, position must therefore be considered to have an important influence in overcoming the usual effect of the pyrone ring in directing the nitro-group to the position 6 Not a trace of the latter could be detected

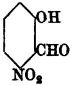
Two places, viz. 5 or 7, thus become possible for the newly entering nitro-group, the alternative structures being as follows:—



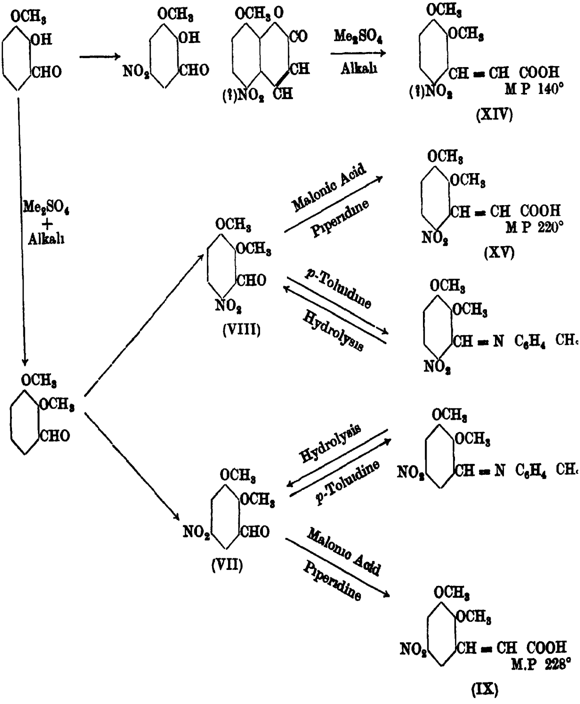


and a final choice between these appeared to be possible through the synthesis

of 6, nitro-ortho-vanillin,



It has been observed that although ortho-vanillin itself gives on direct nitration only the 5, nitro-derivative (VI), its methylation product, ortho-veratric aldehyde, gives a mixture of the 5, (VII), and the 6, nitro-derivatives (VIII), a separation between which is possible by taking advantage of the difference in solubilities of their para-toluidil derivatives (cf. Cain and Simonsen, *J C S.*, *105*, 1914, 159; Robinson, *J C S.*, 1914, 2382; Davies, *J.C.S.*, 1923, 1575; Perkin and Robinson, *J.C S*, 1924, 2355) The reactions are explained by the following scheme:—



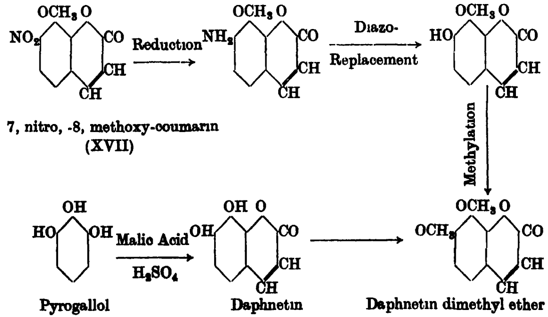
The 6, nitro-ortho-veratric aldehyde (VIII) was prepared in this manner in a yield of 4 grams, starting from 10 grams of ortho-veratric aldehyde

The demethylation of the methoxy groups in the 6, nitro-ortho-veratric aldehyde by the usual methods proved, however, to be exceedingly difficult, only resinous products being obtained in the attempts.

An indirect solution of the problem was then sought in the preparation by Robertson and Cantor's method (*J C S*, 1932, 1181) of the corresponding nitro-2, 3, dimethoxy-cinnamic acid from (IV), and the comparison of the resulting product with that obtained from 6, nitro-ortho-veratric aldehyde (VIII).

This was done, but the products obtained by the two methods were found to be different While the 6, nitro-2, 3, dimethoxy-cinnamic acid (XV), which was prepared in excellent yield from 6, nitro-ortho-veratric aldehyde by heating with malonic acid and piperidine, melted at 220°, the isomeric nitro-2, 3, dimethoxy-cinnamic acid (XIV) prepared from (IV) melted at 140°. Although the possibility of these being stereoisomers of the *cis-trans*-type was not excluded, the difference between the two was presumed at first to be due to a difference in the position of the nitro-group, because the usual methods of conversion of *cis-trans*-isomers by illumination with sunlight, by subjecting to ultraviolet radiation, or by heat failed to bring about any perceptible change in the two nitro-cinnamic acids The presumption seemed, therefore, to be reasonable that the nitration of 8, methoxy-coumarin had led to the occupation by the nitro-group of the only remaining alternative position, viz position 7, in the coumarin ring

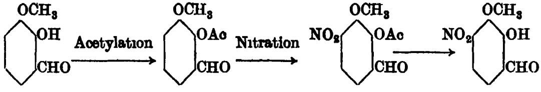
It was hoped at first that a satisfactory proof of the validity of these conclusions could be obtained by preparing from this nitro-body, successively, the amino-, the hydroxy- and the methoxy-derivatives, the last-mentioned product being identifiable with the known Daphnetin dimethyl ether, m p 116° (*Ing Jahresberichte*, 1884, 1786), thus.—



Unexpected experimental difficulties were again encountered here Attempts to replace the NH_2-group by OH by diazotisation did not succeed, although the replacement by chlorine and bromine had previously been accomplished with ease. The experimental details were modified in several ways but without success, a high melting, amorphous and coloured product containing nitrogen and soluble in alkali being invariably obtained The product is believed to be of the nature of a hydroxy-azo-coumarin, but it was not examined further. A similar observation has been recorded by Bignelli (*Gazz*, *27*, II, 1899, 347–357) who experienced great difficulty in diazotising an amino-5, methoxy-coumarin

The third method of attacking the problem which suggested itself was to prepare the 4, nitro-ortho-vanillin (XVI) and then to synthesise therefrom the 7, nitro, 8, methoxy-coumarin (XVII) It is well known that acylated phenolic groups generally have a dominant meta-orienting influence, as is illustrated by the familiar examples of substitutions in ortho- and para-alkyloxy-phenyl esters which are completely controlled by the alkyloxy-group

It was therefore considered possible to direct the nitro-group into the 4, position by starting not with ortho-vanillin, but with ortho-vanillin acetate, thus:—



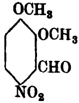
(XVI)

The nitration of ortho-vanillin acetate proceeded smoothly when small quantities were used and the temperature was maintained low, yielding a mono-nitro product which was hydrolysed by alkali or even by standing in contact with water for a day, into a nitro-ortho-vanillin, m p. 92°, (XVI), which was isomeric with but different from 5, nitro-ortho-vanillin, m p 142°

The methylation of this gave a low melting methyl ether which remained liquid at the ordinary room temperature (30°) and was quite distinct in properties from 5, nitro- and 6, nitro-ortho-veratric aldehydes Moreover, it did not form an indigo derivative on treatment with acetone and alkali, which is a characteristic reaction for 6, nitro-ortho-veratric aldehyde and other ortho-nitro-benzaldehydes

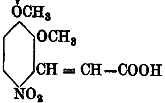
It may be mentioned in this connection that Davies (*J.C S*, 1923, 1575) failed in his attempts to nitrate ortho-vanillin acetate. It is probable that the failure was caused by his working with rather large quantities, for it has been observed that the nitration proceeds smoothly only when small quantities (about 2-3 grams) were employed, whereas with larger quantities the process was difficult to control and oxidation as well as nitration occurred simultaneously. By the usual method of condensation with malonic acid, the 4, nitro-ortho-vanillin methyl ether (XVIII) was converted into a cinnamic acid (XIX), m p 198°, which was found to be different from the two cinnamic acids obtained respectively from 5, and 6, nitro-ortho-veratric aldehydes (cf. Rubenstein, *loc cit*; Perkin and Robinson, *loc. cit.*).

The three possible isomeric nitro-2, 3, dimethoxy benzaldehydes and the corresponding cinnamic acids have thus all been prepared:—



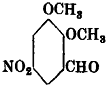
(VIII)

6, Nitro-*o*-Veratric aldehyde



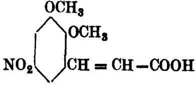
M P 220°

(XV)



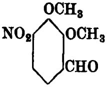
(VII)

5, Nitro-*o*-Veratric aldehyde



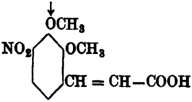
M P. 228°

(IX)



(XVIII)

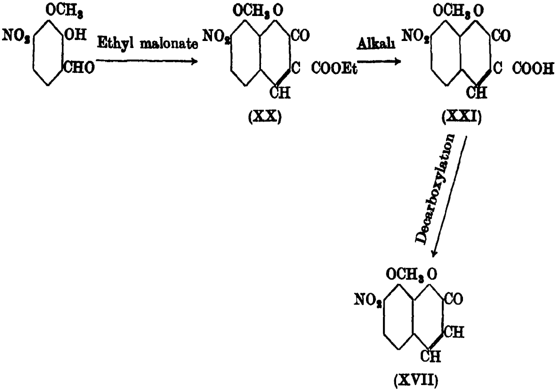
4, Nitro-*o*-Veratric aldehyde



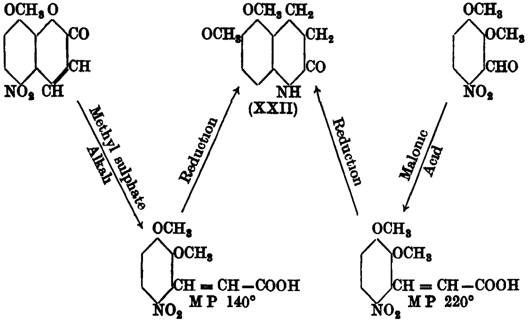
M P 198°

(XIX)

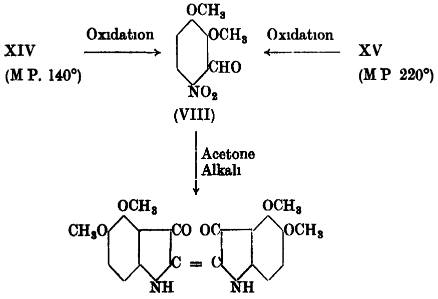
The 4, nitro-ortho-vanillin was finally converted by the Knoevenagel reaction (ethyl malonate and piperidine) into 7, nitro-8, methoxy-coumarin-3, carboxylic ester (XX), m p. 146, which was hydrolysed to the corresponding acid (XXI), m.p 143°, and the latter decarboxylated to 7, nitro-8, methoxy-coumarin (XVII), m.p 164°, which differed from the 6, nitro-8, methoxy-coumarin (V), as well as from the 5 (?), nitro-8, methoxy-coumarin (IV)



It will be seen that all the possible isomeric mononitro-8, methoxy-coumarins have been synthesised, and the positions (6 and 7) of the nitro-group in two of these have been established beyond doubt There remains thus only one possible position, viz , position 5 for the nitro-group in the third compound, i e , that obtained by the direct nitration of 8, methoxy-coumarin The curious difference, however, between the 2, 3, dimethoxy-6, nitro-cinnamic acid, m p 140° (XIV), obtained from what is now known to be 5, nitro-8, methoxy-coumarin by Canter and Robertson's method (*loc cit*) and that, m p 220° (XV), obtained from 6, nitro-ortho-veratric aldehyde by Perkin's process still remained to be explained In the light of the evidence adduced above, the difference could only be accounted for as one of ***stereo-isomerism***, and this view has ultimately been proved to be correct by converting both of these into the same derivatives Thus, on reduction with sodium amalgam, the two different nitro-2, 3-dimethoxy-cinnamic acids (m ps 140° and 220°) were converted into the same 5, 6, dimethoxy-3, 4-dihydro-carbostyril (XXII), m p 174°, the reaction proceeding in the following manner:—



Similarly, on a careful oxidation with potassium permanganate in cold sodium carbonate solution, both the cinnamic acids yielded the same aldehyde which was proved by the melting point and mixed melting point methods, and also by the formation of the indigo derivative to be 6, nitro-ortho-veratric aldehyde, thus —



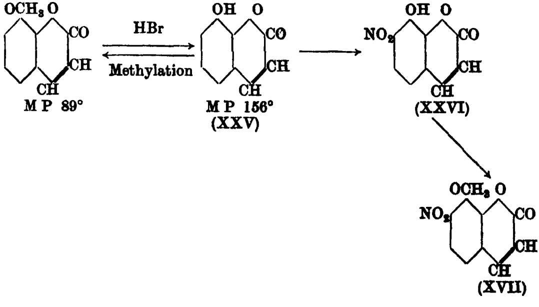
(Indigo-derivative)

In the halogenation of 8, methoxy-coumarin, too, the same influences are found to be at work as in nitration In contrast with the usual rule of the halogen entering the pyrone ring in the first place and then the 6, and the 8 positions in the benzene ring, it is found that the direct halogenation of 8-methoxy coumarin proceeds with substitution exclusively in the benzene ring, not a trace of a pyrone-substitution product being detected by the usual reaction with boiling alkali The position taken up by the halogen atoms was readily fixed by the identity of the products with those obtained from 5, nitro, 8, methoxy-coumarin (IV) by reduction to the amine (X) followed by the diazo-replacement of the amino group by chlorine and bromine atoms. The halogenation of 8, methoxy-coumarin proceeds, therefore, similarly to nitration with the formation of 5, chloro- and bromo-compounds

The influence of the 8, methoxyl group in controlling the entrance of a nitro-group or a halogen atom exclusively into position 5 in the coumarin ring raises the interesting question of how a hydroxyl group in the same position (8) might influence these processes of substitution

Bizzari (*Gazz* , *15*, 1855, 34) claims to have prepared 8, hydroxy-coumarin as a crystalline substance melting at 280°–285° by the condensation of catechol and malic acid in the presence of concentrated sulphuric acid Careful repetition of the work failed to give the desired product, small amounts of a dark amorphous product, which could not be purified, being invariably obtained The desired compound (XXV) was, however, readily prepared in a pure state from 8, methoxy-coumarin by demethylation with hydrobromic acid It melted sharply at 156° and was reconverted by methylation with methyl iodide and silver oxide into the original compound, m p 89° Bizzari's product, m p 280–285°, is, therefore, obviously not 8, hydroxy-coumarin

A mono-nitro-product melting at 222° could be obtained without difficulty from the 8, hydroxy-coumarin by working at a low temperature (ice) and using a mixture of concentrated sulphuric acid and nitric acids. Methylation of this hydroxy nitro-coumarin (XXVI) yielded a nitro-8, methoxy-coumarin which melted at 165° It was thus found to be different from the nitration product of 8, methoxy-coumarin (IV) but identical with the 7, nitro-8, methoxy-coumarin (XVII) prepared previously from 4, nitro-ortho-vanillin



The interesting point that emerges from these studies is that the methoxy- and the hydroxy-groups in position 8 in the coumarin ring direct a newly entering nitro-group to positions 5 and 7 respectively.

EXPERIMENTAL

8, *methoxy-coumarin* (I)

The following conditions were worked out for obtaining the best yield of the coumarin:

Ortho-vanillin (20 g), freshly fused sodium acetate (15 g) and acetic anhydride (35 g) were refluxed for 17 hours at 180°–200° by heating in an electric bath The product of reaction was poured into crushed ice, when a semi-solid product separated The aqueous layer was decanted and the solid was washed with distilled water and quickly stirred with sodium hydroxide (20 c c of 5%) and filtered, the acidic intermediate product being taken up by the alkali (A) The residue was dissolved in alcohol (150 c c), treated with norit charcoal, boiled and concentrated to about a third of its volume, filtered and kept overnight in ice when 8, methoxy-coumarin separated in needles After filtration, the residue was crystallised from water, when pure 8, methoxy-coumarin was obtained The alcoholic filtrate was diluted with water and the oil which separated deposited crystals of 8, methoxy-coumarin on boiling with water, filtering and cooling The oil which remained was again boiled with the mother liquor, filtered and cooled and the process repeated till no more of 8, methoxy-coumarin could be separated M P. 89° Yield, 13 grams

3, *methoxy*-2, *hydroxy-cinnamic acid* (II)

The alkali solution (A), on acidification with dilute hydrochloric acid, gave a voluminous precipitate It was filtered and dried. M P 176° Yield, 1·5 grams

0·1128 g of the acid gave 0 2557 g CO_2 and 0 0532 g H_2O

Found. C, 61·83; H, 5·24 per cent

$C_{10}H_{10}O_4$ requires C, 61·85, H, 5·15 per cent

The methyl ester was prepared by saturating an absolute methanol solution of the acid (1 g) with dry HCl gas White needles M P 106° Yield, 0·8 gram.

0·01101 g of the ester gave 0·2558 g CO_2 and 0 0598 g of water

Found C, 63·25; H, 6 00 per cent

$C_{11}H_{12}O_4$ requires C, 63·46, H, 5 77 per cent

8, *methoxy-coumarin* 3, *carboxylic ester.*

The method described by Robinson (*loc. cit*) was adopted with slight modifications for preparing this compound

7·5 grams of the pure crystallised compound, m p 96°, were obtained from 8 grams of ortho-vanillin, 12 grams of malonic ester and 10 drops of piperidine.

8, *methoxy-coumarin* 3, *carboxylic acid* (III).

The ester (2 g) was refluxed with 2N sodium hydroxide (20 c c.) for one hour on the bare flame When the oily layer had completely disappeared, the red solution was cooled and acidified with dilute HCl The acid which separated crystallised as white needles from alcohol M P. 210° Yield, 1·9 grams

Preparation of 8, *methoxy-coumarin by decarboxylation of* 8, *methoxy-coumarin*-3, *carboxylic acid.*

8, methoxy-coumarin-3, carboxylic acid (1 g) was intimately mixed with a mixture of sand (2 g) and copper powder (2 g) and heated on the bare flame until there was a copious evolution of white fumes The heating was then stopped and the reaction was allowed to complete by itself After the reaction mixture was allowed to cool, it was extracted with absolute alcohol and on removing the solvent by distillation, 8, methoxy-coumarin was left as a residue On crystallising from water it melted sharply at 89° Yield, 0·5 gram

When used in large quantities, the reaction was found to give rise to decomposition products thus reducing the yield considerably

5, *nitro*-8, *methoxy-coumarin* (IV)

8, methoxy-coumarin (10 g) was dissolved in glacial acetic acid (15 c c), and a mixture of fuming nitric acid (5 6 c c) and glacial acetic acid (4 c c) was added drop by drop No rise in temperature was noticed but when concentrated sulphuric acid (10 c c) was added drop by drop there was a gradual rise in temperature The mixture was cooled in running water The pale yellow solid which separated on standing was filtered, washed with plenty of water and dried M P 196-200° It was crystallised from glacial acetic acid from which it separated as long yellow needles M P 206° The mother liquor on pouring into water gave a further quantity of the nitrated product M P 206° Yield, 7 5 grams

0 01654 g of the substance gave 0·92 c c of nitrogen at 33° and 758 mm
Found N, 6·23 per cent
$C_{10}H_7O_5N$ requires N, 6·3 per cent
0·0235 g of the substance gave 0·04669 g CO_2 and 0·00656 g H_2O
Found. C, 54·18, H, 3 1 per cent
$C_{10}H_7O_5N$ requires C, 54·29, H, 3·16 per cent.

5, *amino*-8, *methoxy-coumarin* (X)

A mixture of 5, nitro-8, methoxy-coumarin (2·5 g), pure anhydrous stannous chloride (5 g), granulated tin (5 g), alcohol (5 c.c.) and concentrated HCl (25 c c.) was kept overnight in a stoppered bottle at the room temperature The next day the reaction mixture was shaken in the mechanical shaker for 6 hours. The yellow solid was then allowed to settle, filtered, washed with distilled water and dried on a porous plate in the vacuum desiccator.

It was mixed intimately with double the quantity by weight of a mixture of anhydrous sodium carbonate and crystallised sodium acetate, and extracted with benzene in a Soxhlet apparatus The solid left behind on distilling off the solvent was crystallised from alcohol which deposited yellow needles M P 166° Yield, 0·95 gram

0 1074 g. of the substance gave 6 58 c c of nitrogen at 33° and 766·5 mm
Found: N, 6·92 per cent.
$C_{10}H_9O_3N$ requires N, 7·31 per cent.

The *acetyl derivative* was obtained by rubbing the amine with acetic anhydride, adding a little ice water and recrystallising the product from alcohol M P 265°.

0 02047 g of the substance gave 1·2937 c c of nitrogen at 34° and 760·5 mm
Found. N, 6 14 per cent
$C_{12}H_{11}O_4N$ requires N, 6·0 per cent.

The hydrochloride was prepared by dissolving the amine in hot concentrated HCl and allowing it to cool gradually Long needle-shaped crystals of the hydrochloride separated. M P 205°

0 1920 g of the substance gave 0 1194 g. of AgCl
Found. Cl, 15·39 per cent
$C_{10}H_9O_3ClN$ requires Cl, 15 67 per cent

The picrate, obtained in the usual way by dissolving the amine in HCl by warming and adding a cold saturated solution of picric acid, crystallised from alcohol as yellow rectangular plates M P 179-180°

0·02346 g of the substance gave 2·74 c c of nitrogen at 31° and 762 mm
Found N, 13 2 per cent
$C_{16}H_{12}O_{10}N_4$ requires N, 13·33 per cent.

5, *chloro*-8, *methoxy-coumarin*

A solution of 5, amino-8, methoxy-coumarin (2 g) in 4N HCl (20 c.c.) was cooled to 0° in ice and diazotised with a solution of sodium nitrite (·7 g) in water (10 c.c.). After standing in the ice-bath for half an hour, the cold diazotised solution was added from a separating funnel to an ice cold solution of cuprous chloride (2·2 g.) in strong HCl (15 c.c) The mixture was stirred for a few minutes and then gradually heated on the water-bath until effervescence ceased The precipitate obtained on cooling was filtered, washed with N/10 sodium hydroxide and water, dried and extracted with the minimum quantity of boiling alcohol The alcoholic solution on cooling gave white silky needles. M.P. 182° Yield, 1·2 grams

0·2014 g. of the substance gave 0·1352 g of AgCl
Found: Cl, 16·62 per cent.
$C_{10}H_7O_3Cl$ requires Cl, 16·87 per cent.

5, bromo-8, methoxy-coumarin

A solution of 5, amino-8, methoxy-coumarin (2 g) in HBr (20 c c) was cooled to 0° and diazotised with a cold solution of sodium nitrite (·7 g) in water (10 c c) After standing for half an hour, the cold diazotised solution was added from a separating funnel to an ice-cold solution of cuprous bromide (2 g) in HBr (15 c c) The mixture was stirred for some time and then gradually warmed on the water-bath until effervescence ceased The precipitate obtained on cooling was filtered, dried and extracted with alcohol. The solvent was distilled off and the residue crystallised from alcohol as rhombic plates M P 166° Yield, ·8 gram

0·2133 g of the substance gave 0·1582 g of AgBr.

Found Br, 31·56 per cent

$C_{10}H_7O_3Br$ requires Br, 31·35 per cent

5, cyano-8, methoxy-coumarin

This compound was prepared by treating the diazotised amine (4 g) with a solution of cuprous cyanide (KCN, 4 g , crystallised copper sulphate 3·5 g , and water 20 c.c) at 50° The mixture was heated at 100° for an hour The solid collected was extracted repeatedly with boiling rectified spirit The solvent was distilled off and two crystallisations of the residue from alcohol furnished the cyano compound as fine colourless needles M P 175° Yield, 1·1 grams

0·1030 g. of the substance gave 5·6 c c. of nitrogen at 31° and 766·5 mm.

Found: N, 6·95 per cent.

$C_{11}H_7O_3N$ requires N, 6·915 per cent.

Quinaldino-7, 8-α, pyrone (XII)

A mixture of 5, amino-8, methoxy-coumarin (4 g) and fuming HCl (2·5 c c) was cooled in ice, saturated with HCl and left overnight. The dark viscous product was heated on an oil-bath for 3 hours to a temperature of 130–140°. It was cooled and extracted with small quantities of boiling water. The combined extracts were cooled in ice and made alkaline with sodium bicarbonate. The yellow flocculent precipitate was filtered and dried This was dissolved in boiling water and a few drops of alcohol The solution on cooling gave a white precipitate which was filtered and dried It separated from alcohol as white crystals M P 217-218°. Yield, 0·19 gram.

0·02459 g of the substance gave 1·18 c c. of nitrogen at 760 mm. and at 30°C.

Found: N, 6·04 per cent.

$C_{14}H_{11}O_3N$ requires N, 5·81 per cent.

Attempts to oxidise the 5, nitro-8, methoxy-coumarin.

5, nitro-8, methoxy-coumarin (2 g.) was dissolved in the minimum amount of caustic soda (N/10). Normal aqueous permanganate was added to the solution with vigorous shaking after each addition. The permanganate was reduced rapidly The solution was warmed on the water-bath and the addition of the permanganate was continued until a permanent pink colour was noticed The solution was filtered from manganese dioxide and the filtrate was cleared by passing sulphur dioxide Nothing separated out even on concentrating the solution It was evaporated completely to dryness and extracted first with alcohol and then with benzene Nothing was taken up by either benzene or alcohol. The same experiment was repeated in the cold, sulphur dioxide being passed without the precipitate of manganese dioxide being filtered off The white solid which separated out completely dissolved on boiling with concentrated HCl and on cooling the clear solution a white crystalline substance melting at 106° was obtained. This substance was identified as oxalic acid. Yield, 1 9 grams

The mother liquor was evaporated to dryness and extracted with both alcohol and benzene, but on distillation of the solvent no residue was left

The same oxidation was carried out in acetone medium but without success

Action of alkali on 5, nitro-8, methoxy-coumarin

5, nitro-8, methoxy-coumarin (1 g) was dissolved in sodium hydroxide (20 c c) and boiled for half an hour The red solution on acidification gave the unchanged material melting at 205°.

6, *nitro-2, 3, dimethoxy-cinnamic acid* (XIV)

For the preparation of this compound the method adopted by Robertson and Cantor (*loc. cit*) was employed

5, nitro-8, methoxy-coumarin (4 g) in methanol (30 c c) and 20% sodium hyroxide (20 c.c) was refluxed till the fission of the pyrone ring was complete as shown by the clear liquid not giving any precipitate on dilution The warm solution was agitated with methyl sulphate (80 g) and 20% sodium hydroxide (15 c.c). The reaction mixture was kept undisturbed and allowed to cool. It was filtered from mechanical impurities and acidified with dilute HCl The greyish precipitate was filtered, dried and crystallised from alcohol. Pale yellow needles. M P 140°. Yield, 4 grams

0·1004 g of the acid gave 5 c c. of nitrogen at 31°C and 766 25 mm

Found: N, 5·52 per cent.

$C_{11}H_{11}O_6N$ requires N, 5·54 per cent.

The silver salt of the acid was prepared and analysed. 0·1860 g of the silver salt gave on ignition 0·0550 g. of silver The equivalent weight of the acid = 258·08.

$C_{11}H_{11}O_6N$ requires M W , 253

Action of sunlight on the cinnamic acid

The cinnamic acid (0·5 g.) was dissolved in chloroform and exposed to direct sunlight in a quartz flask for 12 hours. On removing the solvent, the unchanged acid was recovered

Effect of heat on the cinnamic acid.

The cinnamic acid (0·1 g) was heated in a test tube in a sulphuric acid-bath to 190°. The acid melted and was kept at this temperature for an hour On cooling, the solidified product was scraped off and crystallised from glacial acetic acid M P 140° Thus only unchanged material was recovered

5, *nitro-ortho-vanillin* (VI)

Ortho-vanillin (30 g) was dissolved in glacial acetic acid (120 c c) and concentrated nitric acid (15 c c) was added drop by drop The reaction mixture was well cooled by means of ice and salt There was considerable evolution of heat, but the temperature was always kept below 5°. The yellow nitrated product which separated on standing was filtered, washed well with water, and crystallised from glacial acetic acid The mother liquor on the addition of water gave a further quantity of the 5, nitro-ortho-vanillin which separated from glacial acetic acid as long yellow needles. M.P 142° Yield, 31·5 grams.

6, *nitro*-8, *methoxy-coumarin* (V)

5, nitro-ortho-vanillin (12 g), pure acetic anhydride (18 g) and freshly fused sodium acetate (8 g) were refluxed continuously for 17 hours at a temperature of 180–200° with the exclusion of moisture The clear liquid was poured into crushed ice and the solid collected was filtered, washed with water and 5% sodium bicarbonate and finally with ether. Two crystallisations from glacial acetic acid furnished faintly brown needle-shaped crystals of 6, nitro-8, methoxy-coumarin melting at 203° Yield, 5·5 grams.

0·03239 g of the substance gave 1·83768 g. of nitrogen at 34° and 760 mm.
Found. N, 6·45 per cent.
$C_{10}H_7O_5N$ requires N, 6·3 per cent
0·01565 g of the substance gave 0·03105 g CO_2 and 0·00437 g. H_2O.
Found· C, 54·12; H, 3·10 per cent.
$C_{10}H_7O_5N$ requires C, 54·29; H, 3·16 per cent.

6, *amino*-8, *methoxy-coumarin* (XI).

6, nitro-8, methoxy-coumarin (2·5 g) was mixed well with anhydrous stannous chloride (5 g), granulated tin (5 g.), alcohol (5 c.c.) and concentrated HCl (25 c.c.) and kept overnight in a stoppered bottle at the room temperature. The next day it was shaken in the mechanical stirrer for 6 hours. The solid was allowed to settle, filtered and washed well with distilled water. It was dried on a porous plate in a vacuum desiccator. The solid weighing nearly

3·5 g. was intimately mixed with crystalline sodium acetate (7 g) and anhydrous sodium carbonate (7 g) and extracted with chloroform in a Soxhlet apparatus. The solvent was distilled off and the residue of yellow solid crystallised from dilute alcohol M.P 167° Yield, 1 1 grams

0·01095 g of the substance gave 0 68 c c of nitrogen at 34° and 762 mm.
Found N, 6·96 per cent
$C_{10}H_9O_3N$ requires N, 7 3 per cent

The *acetyl derivative* was prepared by rubbing the 6, amino-8, methoxy-coumarin with acetic anhydride and pouring on to crushed ice M P 241°

0 02135 g of the substance gave 1·15 c c of nitrogen at 34° and 762 mm.
Found N, 6 0 per cent
$C_{12}H_{11}O_4N$ requires N, 6 0 per cent

The picrate was prepared by dissolving the amino in warm, dilute HCl and adding a cold saturated solution of picric acid It crystallised from alcohol as long yellow needles M P 228°

0·01555 g of the substance gave 1 85 c c of nitrogen at 32° and 763 mm.
Found. N, 13 42 per cent
$C_{16}H_{12}O_{10}N_4$ requires N, 13·33 per cent

The hydrochloride was obtained as yellow needles M P 255°

0·3339 g of the substance gave 0 2134 g of AgCl
Found. Cl, 15 82 per cent.
$C_{10}H_9O_3ClN$ requires Cl, 15 67 per cent

6, *chloro*-8, *methoxy-coumarin.*

6, amino-8, methoxy-coumarin (2 g) in 4N HCl (20 c c) was cooled to 0° and diazotised with a solution of sodium nitrite (·7 g) in water (10 c c) After standing in the ice-bath for half an hour the cold solution was added from a separating funnel to an ice-cooled solution of cuprous chloride (2 2 g) in strong HCl (15 c c) The mixture was stirred for a few minutes and then gradually heated on the water-bath until effervescence ceased The precipitate obtained on cooling was filtered, washed with N/10 sodium hydroxide, and then with water, dried and extracted with the minimum quantity of boiling alcohol. On distilling off the solvent, the chloro compound separated as pale yellow needles M P 121-122°

0·2267 g of the substance gave 0 1552 g of AgCl
Found Cl, 16 93 per cent.
$C_{10}H_7O_3Cl$ requires Cl, 16 87 per cent

6, *bromo*-8, *methoxy-coumarin*

A well-cooled solution of 6, amino-8, methoxy-coumarin (2 g.) in HBr (20 c.c.) was diazotised with a cold solution of sodium nitrite (·7 g.) in water (10 c.c.) After an hour, the cold solution was added from a dropping funnel to an ice-cooled solution of cuprous bromide (2 g.) in HBr (15 c.c.). The mixture was stirred for some time and then gradually warmed on the water-bath until effervescence ceased The precipitate obtained on cooling was filtered, dried and extracted with alcohol The solvent was distilled off and the residue, on crystallisation from alcohol, gave pale brown needles of the bromo compound M P 115°

0·2910 g of the substance gave 0·2135 g of AgBr

Found. Br, 31 21 per cent

$C_{10}H_7O_3Br$ requires Br, 31·35 per cent

Quinaldino-6, 5-α-pyrone (XIII)

A mixture of 6, amino-8, methoxy-coumarin (1 g), fuming HCl (2·5 c c) and paraldehyde (2 c c) was cooled in ice, saturated with dry HCl gas and left overnight Next morning the dark viscous liquid was heated in an oil-bath to a temperature of 130°–140° for 3 hours The solid was crushed and extracted with boiling water, cooled in ice and made alkaline with solid sodium bicarbonate The yellow precipitate which separated was crystallised from hot dilute alcohol M P 237° Yield, ·3 gram

0·03256 g of the substance gave 1·65 c c of nitrogen at a temperature of 33° and 762 5 mm

Found N, 5·7 per cent.

$C_{14}H_{11}O_3N$ requires N, 5·8 per cent

5, nitro-2, 3, dimethoxy-benzaldehyde (VII)

5, nitro-ortho-vanillin was not conveniently methylated by means of methyl sulphate and alkali or methyl iodide and alkali In both cases the unreacted product was recovered The methylation was best carried out by the application of Purdie's method

5, nitro-ortho-vanillin (7 4 g) dissolved in a mixture of methyl iodide (5 c c) and chloroform (30 c c) was boiled with finely powdered silver oxide (7 g) for 3 hours The inorganic matter was filtered off and most of the solvent removed when the methylated product separated This was crystallised from methyl alcohol. M P 115° Yield, 4·5 grams

5, nitro-2, 3, dimethoxy-cinnamic acid (IX)

The following method was found to give a better yield than the one employed by Rubenstein (*loc cit.*):

A mixture of 5, nitro-ortho-veratraldehyde (5 g), malonic acid (5 g.), pyridine (10 c.c.) and piperidine (8 drops) was refluxed on the water-bath for 2 hours There was copious evolution of carbon dioxide. The mixture was afterwards heated on the free flame for 10 minutes The reaction mixture was allowed to attain the room temperature, poured into ice water and the excess of pyridine was fixed by means of dilute HCl. The voluminous white precipitate which melted at 224°–226° was crystallised from glacial acetic acid. M.P. 228°. Yield, 4·2 grams.

The ethyl ester was prepared by dissolving the above acid (1 g) in absolute alcohol (20 c c) and saturating with a stream of dry HCl gas The solution was kept overnight corked in a flask The crystals which separated on pouring the liquid into water were collected and dried M P 111°

2, 3, *dimethoxy-benzaldehyde*

In a three-necked flask a mixture of ortho-vanillin (91 g) and water (225 c c) were heated on the steam-bath and a solution of sodium hydroxide (90 g) in water (180 c c) was heated to about 100° and added in one lot to the hot mixture of ortho-vanillin and water The flask was now fitted with a reflux condenser, a mechanical stirrer and a separating funnel Heating was continued on the water-bath, and dimethyl sulphate (94 g) was added through a separating funnel just rapidly enough to maintain ebullition which started after the addition of the first 10–15 c c After the addition of all the dimethyl sulphate, which required about three-quarters of an hour, was over, the reaction mixture was heated for 45 minutes longer and an additional portion of dimethyl sulphate (20 g) was added at the same rate as the first portion At the end of this addition the reaction mixture showed an acid reaction to litmus After ten minutes' heating the reaction mixture was rendered alkaline by the addition of the same solution of sodium hydroxide (30 c c), and another portion of dimethyl sulphate (20 g) added The alternate addition of sodium hydroxide solution and of dimethyl sulphate was repeated until a total quantity of 172 grams of dimethyl sulphate had been added The reaction mixture was finally made alkaline by the addition of 75 c c of sodium hydroxide and heated for 20 minutes On cooling rapidly, the ortho-veratric aldehyde separated as a solid Yield, 95 grams

Nitration of 2, 3, *dimethoxy-benzaldehyde* (cf Davies, *loc cit*).

2, 3, dimethoxy-benzaldehyde (15 g) was dissolved in the requisite amount of glacial acetic acid and 20 c c of concentrated nitric acid (D, 1 4) was added drop by drop No rise of temperature was noticed but a definite reaction took place only when the mixture was heated on the water-bath for about 10 minutes On standing for half an hour, the nitrated product, which was a mixture of 6, and 5, nitro-2, 3-dimethoxy-benzaldehydes, separated out M P 88° Yield, 16 grams

The separation of 6, *nitro*-2, 3, *dimethoxy-benzaldehyde from the mixture of* 5, *and* 6, *nitro*-2, 3, *dimethoxy-benzaldehydes* (cf Perkin, *loc cit*)

The mixture of 5, and 6, nitro-2, 3, dimethoxy-benzaldehydes (21·1 g) was heated with para-toluidine (10·7 g) on the steam-bath until water was seen to separate Sufficient alcohol was then added and the mixture heated until complete solution occurred On cooling, 5, nitro-2, 3, dimethoxy-benzylidine-*p*-toulidil separated first and then the 6, nitro-derivative These substances could be completely purified by careful fractional crystallisation from alcohol The 5, nitro-2, 3, dimethoxy-benzylidine-*p*-toulidil melted at 143° as distinct from the 6, nitro-derivative which melted at 104° By the hydrolysis of these derivatives by means of hot concentrated HCl, the corresponding aldehydes were obtained in quantitative yields The 6, nitro-2, 3, dimethoxy-benzaldehyde melted at 110° whereas the 5, nitro-2, 3, dimethoxy-benzaldehyde melted at 115° The curious observation was made that a mixture of the two in about equal amounts melted sharply at 88°

Attempts to obtain the 6, nitro-ortho-vanillin by the demethylation of 6, nitro-ortho-veratric aldehyde, both by the method of heating in glacial acetic acid solution with (*a*) HBr and (*b*) anhydrous aluminium chloride, ended in failure Only unpurifiable brown, resinous products were obtained

Similarly, attempts to close the coumarin ring by heating the ethyl ester of 6, nitro-2, 3, dimethoxy-cinnamic acid by means of hydriodic acid were also unsuccessful The dark tarry residue was washed with sulphurous acid when it became lighter in colour but it could not be obtained in a pure crystalline state

2, benzene-sulphonyl-3, methoxy-benzaldehyde (cf Rupp and Linck, *loc cit*)

Ortho-vanillin (10 g) was treated with a 15% solution of sodium hydroxide (30 c c) and benzene sulphonyl chloride (14 g), and the mixture shaken in a mechanical shaker for one hour The reaction product was then poured into water when the benzene-sulphonyl-derivative separated as a white solid It crystallised from alcohol in colourless glistening plates M P 121° Yield, 10·5 grams

6, nitro-2, benzene sulphonyl-3, methoxy-benzaldehyde (cf Davies, *loc cit*)

The benzene sulphonyl derivative (1 g) was dissolved in fuming nitric acid (20 c c) The temperature was not allowed to rise above 0° by keeping the solution in an ice-bath After 10 minutes it was poured into water when the benzene sulphonyl 6, nitro-derivative separated as a white solid It crystallised from rectified spirit as pale yellow needles M P 145°

Several attempts were made to remove the benzene sulphonyl group in this derivative, by hydrolysis with (*a*) concentrated hydrochloric acid and (*b*) caustic alkali, but in all cases the experiments failed to give the desired 6, nitro-ortho-vanillin, the benzene sulphonyl derivative being apparently decomposed in the process Again, on condensing the same 6, nitro-3, methoxy-2, benzene sulphoxy-benzaldehyde with malonic acid in the presence of pyridine and piperidine, refluxing for 2 hours, pouring into water and acidifying with HCl, a brown neutral product was obtained which could not be purified by crystallisation

6, nitro-2, 3, dimethoxy-cinnamic acid (m p 220°) (XV)

6, nitro-2, 3, dimethoxy-benzaldehyde (7·5 g) was mixed with malonic acid (4·3 g), pyridine (10 c c) and piperidine (0·1 c c) and was heated on the water-bath for about 2 hours and finally on the sand-bath for 15 minutes, after which it was poured into ice-cold dilute hydrochloric acid and stirred The solid was ground well with a solution of sodium carbonate and filtered The filtrate on acidification deposited 6, nitro-2, 3, dimethoxy-cinnamic acid which came down as long needles on crystallisation from alcohol M P. 220°. Yield, 1 5 grams.

Action of sunlight on 6, nitro-2, 3, dimethoxy-cinnamic acid

The cinnamic acid (1 g) in benzene (10 c c) was exposed to sunlight in a quartz flask for 12 hours On removing the solvent the unchanged material melting at 220° was recovered

Action of heat on 6, nitro-2, 3, dimethoxy-cinnamic acid

The cinnamic acid was heated at 240° in a test tube in a sulphuric acid bath, and the molten substance kept at this temperature for an hour The product was found to be unchanged material melting at 220°

Acetylation of ortho-vanillin (cf Rupp and Baeyer, *loc cit*)

Ortho-vanillin (10 g) was dissolved in a mixture of acetic anhydride (7 5 g.) and pyridine (10 g) and kept undisturbed at the room temperature for 24 hours On diluting with water, the acetyl derivative separated in transparent leaflets. M P. 76° Yield, 11 5 grams

4, *nitro-ortho-vanillin* (XVI)

Careful nitration of ortho-vanillin acetate in small quantities at a time yielded a mixture of the 4, and the 6, nitro-ortho-vanillins A series of experiments conducted for this purpose led to the working out of the following ideal conditions for obtaining the best yield of the nitro compounds

To a mixture of 10 c c of fuming nitric acid (D = 1 40) and 2 c c of concentrated sulphuric acid, cooled to −6°C., was added 3 grams of finely powdered ortho-vanillin acetate, in small quantities at a time, with brisk mechanical stirring During the addition which lasted from 20 to 30 minutes, the temperature was maintained below 0°C. and the stirring continued for another 15 minutes The reaction mixture was then poured into 20 grams of crushed ice when a viscous oil separated at the bottom which was extracted thrice with 20 c c of benzene each time The benzene layers were combined, washed twice with ice-cold water and then shaken up with 5% ice-cold sodium bicarbonate solution till the washings were alkaline, and again washed twice with ice-cold water The benzene was distilled off and the brown oily residue heated to boiling with 20 c c. of 2% NaOH, cooled and acidified with hydrochloric acid The separating yellowish brown solid was a mixture of 4, and 6, nitro-ortho-vanillins It was filtered, washed and dissolved in the minimum quantity of hot glacial acetic acid. Long yellow needles of 4, nitro-ortho-vanillin separated out first M P 92-93° Yield, 1·10 grams

The 6-nitro-ortho-vanillin comes down from the filtrate on careful dilution M P 71-72° Yield, 0·35 gram

0·0914 g of the 4, nitro-ortho-vanillin (m p 92-93°) gave 6 c c of nitrogen at 30°C. and at 762 mm

Found N, 7 26 per cent

$C_8H_7O_5N$ requires N, 7·11 per cent

Acetic acid is found to be a better solvent than alcohol for this separation of the 4, and 6, nitro-derivatives

The 6, nitro-compound gives a dark red solution with ferric chloride and forms a low melting acetyl derivative A little was warmed with acetone and the solution poured in a thin stream into dilute potassium hydroxide solution when a dark blue colour was produced showing that the nitro-group was in the ortho-position to the aldehyde group

7, *nitro*-8, *methoxy-coumarin* 3, *carboxylic ester* (XX)

4, nitro-ortho-vanillin (2 g), malonic ester (3 g) and piperidine (4 drops) were heated on the water-bath for 15 minutes and kept overnight tightly corked in a flask A brown semi solid mass separated the next day on pouring the reaction product into water containing dilute HCl On washing with dilute alcohol a pale yellow solid was obtained which crystallised from alcohol as long needles M P 146° Yield, 1 gram

0·03415 g of the substance gave 1·45 c c of nitrogen at 32° and 760 mm

Found N, 4 8 per cent

$C_{13}H_{11}O_7N$ requires N, 4·7 per cent

7, *nitro*-8, *methoxy-coumarin* 3, *carboxylic acid* (XXI).

The ester (1 g) was hydrolysed with 2N sodium hydroxide (8 c c) by refluxing for half an hour on the water-bath The red solution was filtered from mechanical impurities, cooled and acidified The voluminous precipitate was filtered, dried and crystallised from glacial acetic acid M P 146° Yield, 0·9 gram

0·01376 g of the substance gave 0·63 c c of nitrogen at 33° and 764 mm

Found. N, 5·11 per cent

$C_{11}H_7O_7N$ requires N, 5·29 per cent.

7, *nitro*-8, *methoxy-coumarin* (XVII)

7, nitro-8, methoxy-coumarin 3, carboxylic acid (1 g) was intimately mixed with copper powder (2 g) and washed fine sand (2 g.) and heated directly on the flame until white fumes evolved copiously when the heating was stopped and the reaction allowed to complete itself The cold mass was extracted with absolute alcohol which left on evaporation a pale brown solid. This was washed with dilute bicarbonate solution and then crystallised twice from dilute alcohol. Short thick needles. M.P. 164-65°. Yield, 0·5 gram.

0·01345 g. of the substance gave 0·74 c.c. of nitrogen at 33° and 760 mm.
Found. N, 6·2 per cent.
$C_{10}H_7O_5N$ requires N, 6·3 per cent.

6, nitro-2, 3, dimethoxy benzaldehyde (*By oxidation of* 6, *nitro*-2, 3, *dimethoxy-cinnamic acid.*)

6, nitro-2, 3, dimethoxy-cinnamic acid (1 g.) prepared from 5, nitro-8, methoxy-coumarin by Robertson's method was suspended in water (40 c.c.) and a little sodium carbonate solution (2 c.c.) was added and stirred until it went into solution. The solution was taken in a separating funnel, mixed with benzene (100 c.c.) and treated with a cold solution of potassium permanganate (1·48 g. in 25 c.c. of water), the mixture being vigorously shaken and cooled after each addition. When the addition of potassium permanganate was completed the mixture was allowed to remain for a few minutes, then filtered and the precipitate of manganese dioxide washed with benzene. The benzene layer was separated from the aqueous layer, dried over sodium sulphate and the solvent removed by distillation when a brownish residue was left behind. On crystallisation from a mixture of benzene and ligroin it melted sharply at 110°. It gave the expected indigo derivative with acetone and sodium hydroxide and was finally identified with an authentic specimen of 6, nitro-2, 3-dimethoxy-benzaldehyde by a mixed melting point determination.

0·01334 g. of the substance gave 0·78 c.c. of nitrogen at 33° and 762 mm.
Found. N, 6·57 per cent.
$C_9H_9O_5N$ requires N, 6·63 per cent.

5, 6, dimethoxy-3, 4, *dihydro-carbostyril* (XXII)

The acid m.p. 140° (1 g.) was dissolved in the minimum amount of 2N sodium hydroxide and reduced by means of 4% sodium amalgam (30 g. of mercury and 1·2 g. of sodium). The addition of sodium amalgam was so adjusted as not to produce much heat during the process. The solution was kept just alkaline by the addition of acetic acid to neutralise the excess of alkali formed and kept undisturbed for an hour. The mercury was tapped off and the solution acidified with acetic acid. As no precipitate was formed, the solution was extracted thrice with ether, the ethereal extract dried over sodium sulphate and the ether distilled off. The oily residue that was left behind solidified on cooling in ice and rubbing with a rod. After washing with dilute sodium carbonate and crystallising from alcohol, pale brown crystals, m.p. 173°, were obtained. Yield, 0·45 gram. The crystals dissolved in dilute HCl and were reprecipitated by ammonia.

0·01889 g. of the substance gave 1·166 c.c. of nitrogen at 35° and 759 mm.
Found: N, 6·71 per cent.
$C_{11}H_{13}O_3N$ requires N, 6·77 per cent.

5, 6, dimethoxy-3, 4, dihydro-carbostyril. (*From dimethoxy-cinnamic acid, m p. 220°,* (XV), *prepared from* 6, *nitro-ortho-veratric aldehyde*)

6, nitro-2, 3, dimethoxy-cinnamic acid, m p 220°, (1·5 g) was dissolved in 2N sodium hydroxide (20 c c) and treated with 4% sodium amalgam in the same way as in the previous case The reaction mixture was kept faintly alkaline by the addition of acid from time to time After addition was complete, the reaction mixture was allowed to stand for an hour, the mercury was tapped off, and the aqueous layer filtered from the precipitate formed The precipitate crystallised from alcohol in shining plates melting at 174° The alkaline filtrate was made just acidic, basified again with ammonia and evaporated to dryness The dried mass on extraction with alcohol gave some more of the carbostyril Total yield, 1 1 grams This gave no depression in melting point when mixed with a specimen of the previous product prepared by the reduction of the isomeric 6, nitro-2, 3, dimethoxy-cinnamic acid M P. 140°

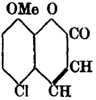
0·015 g. of the substance gave 0·00683 g of carbon dioxide and 0 0273 g. of water.

Found: C, 63 1; H, 6·1 per cent

$C_{11}H_{13}O_3N$ requires C, 63 2; H, 6·2 per cent.

Halogenation of 8, *methoxy-coumarin.*

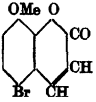
*5, chloro-*8, *methoxy-coumarin*



8, methoxy-coumarin (2 g) was dissolved in glacial acetic acid (20 c c) and chlorine gas from a cylinder was passed into the solution There was considerable evolution of heat. After some time crystals of 5, chloro-8, methoxy-coumarin began to separate. It was filtered and dried M P 182°. Yield, 1·8 grams.

The melting point was not depressed when mixed with a specimen of 5, chloro-8, methoxy-coumarin obtained from 5, nitro-8, methoxy-coumarin by reduction, diazotisation and replacement of the diazo group by chlorine.

*5, bromo-*8, *methoxy-coumarin.*



8, methoxy-coumarin (1 g) was dissolved in glacial acetic acid (20 c c.) and bromine (1·1 c c) in acetic acid (10 c c) was added drop by drop There was considerable heat evolved accompanied by the evolution of HBr gas After standing for 15 minutes and cooling in ice, the 5, bromo-8, methoxy-coumarin was collected and crystallised from acetic acid M P 167° No depression in this melting point was observed on admixture with a specimen of 5, bromo-8, methoxy-coumarin prepared from 6, nitro-8, methoxy-coumarin by reduction, diazotisation and replacement of the diazo group by bromine.

Nitration of 8, *hydroxy-coumarin*

8, ***hydroxy-coumarin*** (XXV)

8, methoxy-coumarin (8 8 g) in glacial acetic acid (25 c c) was mixed with hydrobromic acid (2 7 c c) (D = 1 5) and refluxed for 6 hours The product of reaction was diluted with water (25 c c) and just neutralised with sodium bicarbonate solution The hydroxy compound which separated was filtered, and crystallised from boiling water Clusters of fine needles M P 156° The neutral mother liquor on evaporation to dryness and extraction with absolute alcohol gave some more of the hydroxy compound Yield, 7 grams

0·03506 g of the substance gave 0 08549 g of carbon dioxide and 0·0112 g of water

Found C, 66 5; H, 3·55 per cent

$C_9H_6O_3$ requires C, 66 6, H, 3 6 per cent

Attempts to synthesise 8, hydroxy-coumarin from catechol and malic acid by the method given by Bizzari (*loc cit*) were unsuccessful

8, ***hydroxy*-7, *nitro-coumarin*** (XXVI)

8, hydroxy-coumarin (1 1 g) was added to a mixture of concentrated nitric acid (1·2 c c) and concentrated sulphuric acid (1·2 c c), the temperature being kept within a range of 0–5° by keeping it in an ice-bath After the addition was completed the reaction mixture was kept at the same temperature for an hour with stirring and the pasty mass then thrown into water. The nitrated product which separated was washed with water and 5% sodium bicarbonate solution (10 c c), filtered, dried and crystallised from glacial acetic acid. Yellow plates melting at 224°

0·0204 g. of the substance gave 1 19 c c of nitrogen at 33° and 762 mm.

Found: N, 6·52 per cent

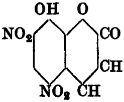
$C_9H_5O_5N$ requires N, 6 76 per cent.

8, ***methoxy*-7, *nitro-coumarin.***

8, hydroxy-7, nitro-coumarin (0 2 g) was suspended in dried chloroform (20 c.c.) containing freshly precipitated silver oxide (0·2 g.) also in suspension and methyl iodide (2 c c.) The mixture was refluxed for 2 hours and filtered hot. The filtrate, on evaporation, deposited 7, nitro-8, methoxy-coumarin which crystallised from alcohol in needles melting at 164°. From the silver oxide residue a small quantity of the unreacted hydroxy-compound was recovered. 7, nitro-8, methoxy-coumarin gave no depression in melting point by admixture with a specimen of the synthetic compound from 4, nitro-ortho-vanillin.

0·01345 g. of the substance gave 0·74 c.c. of nitrogen at 33° and 760 mm.
Found: N, 6·2 per cent
$C_{10}H_7O_5N$ requires N, 6·3 per cent

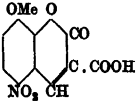
Dinitro-8, hydroxy-coumarin (*Nitration at ordinary temperature.*)



8, hydroxy-coumarin (·5 g.) was dissolved in glacial acetic acid (3 c.c.), and a mixture of fuming nitric acid (1 c c) and glacial acetic acid (5 c c) was added drop by drop There was no appreciable rise in temperature, but on the addition of concentrated sulphuric acid (1 c c) there was much evolution of heat The mixture was cooled in running water when a yellow solid separated which crystallised from glacial acetic acid in yellow needles. M P. 196°. Yield, 0·6 gram.

0·2187 g. of the substance gave 2·17 c c. of nitrogen at 34·5° and 758 mm.
Found. N, 11·10 per cent.
$C_9H_4O_7N_2$ requires N, 11·11 per cent.

Nitration of 8, *methoxy-coumarin*-3, *carboxylic acid.* (5, *nitro*-8, *methoxy-coumarin*-3, *carboxylic acid.*)



8, methoxy-coumarin-3, carboxylic acid (5 g.) was dissolved in concentrated nitric acid (20 c c) at the ordinary temperature. It was then warmed on the water-bath for 10 minutes and kept undisturbed for 2 hours On pouring into water pale yellow crystals of the nitro compound separated. M.P. 203°.

0·012 g. of the substance gave 0·55 c.c. of nitrogen at 33° and 760 mm.
Found: N, 5·13 per cent.
$C_{11}H_7O_7N$ requires N, 5·29 per cent.

5, nitro-8, methoxy-coumarin. (By decarboxylation of the above nitro-acid.)

5, nitro-8, methoxy-coumarin-3, carboxylic acid (3 g) was mixed with sand (2 g) and copper powder (2 g) and heated on the free flame until there was evolution of white fumes When the reaction had subsided, the reaction mixture was cooled, extracted with alcohol and the residue obtained on distilling off the alcohol was crystallised from dilute alcohol It separated as long white needles, M P. 205°, and showed no depression in melting point when mixed with a specimen of 5, nitro-8, methoxy-coumarin obtained by the nitration of 8, methoxy-coumarin

PRESIDENCY COLLEGE,
MADRAS,
July 16th, 1940.

MEASUREMENT OF COEFFICIENT OF REFLECTION AND PHASE FOR SOUND WAVES

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(Communicated by Dr R N Ghosh, D Sc, F N I)

(*Read August* 20, 1940)

INTRODUCTION

The problem of the absorption of sound in porous materials has been investigated both theoretically and experimentally by several investigators[1] in this laboratory during recent years The present paper carries this work a stage further in that the phase change associated with reflection from porous substances is studied by measuring the effect of air load on the electrical impedance of the sound source So far no data seem to be available regarding the change of phase that takes place on reflection from different substances and it is also not definitely known whether it is possible to alter the coefficient of reflection without any appreciable change of phase It is well known that if there is a surface of separation between the two sides of a tube through which sound waves are passing then (1) a part of the waves will be transmitted and (2) a part will be reflected back and the reflected wave will undergo a change of phase depending upon the nature of the partition In the absence of the partition there is no reflection and no reflected wave If the barrier is rigid, perfect reflection takes place and the change of phase is π But nothing is known about phase change between the reflection coefficients zero and one The present work was undertaken to investigate this point in particular and also to determine the coefficients of absorption for sound of different materials

The method in brief is a modification of that used by Fay and Hall[2] for measuring the acoustical output of a telephone receiver It consists in measuring the electrical impedance of a telephone receiver which is acoustically connected to an air column The other end of this air column is fitted with a piston When the receiver works, the air column vibrates It reacts upon the receiver and alters its electrical impedance This change is measured by a suitable apparatus The coefficient of reflection and the corresponding phase change is calculated from the constants of the receiver and the reactance and resistance terms of the electrical impedance The measurement of phase simultaneously with the coefficient of reflection has been made possible, since both the reactance and resistance terms are determined separately by this method.

Published December 9th, 1940.

The paper is divided into three parts:—

1. The first part deals with the theoretical background necessary to enable one to determine the quantities to be measured for evaluating the resistance and the reactance terms of a reflector.
2. The second part describes the experimental arrangement, the sound source, etc., the observations and graphs for the determination of sound absorption coefficients of *ad hoc* materials and the consequent phase changes at reflection. The sources of error in the measurements are also discussed in this section.
3. The third section is devoted to the determination of absorption coefficients of an assemblage of fine tubes, and the phase change that takes place from the surface of the tubes This assemblage is similar to any sound absorbing material of which the physical constants are known.

PART I

1. *Theory of the moving coil receiver unit*[3]

When a cylindrical coil having n number of turns is situated in a radial magnetic field of intensity H gauss, the force is given by

$$F = \frac{2\pi b i H n}{10} = Ki$$

where b is the radius of the coil

The back electromotive force generated when the coil moves to and fro cutting the magnetic lines of force will be

$$e = 2\pi b H \frac{\delta x}{\delta t} n$$

where δx denotes the distance moved by the coil in time δt

$$e = 2\pi b H \dot{x} n = K\dot{x}$$

If E be the total input e.m f , then $E = e + Z_{EW} i$,
Z_{EW} being the electrical impedance of the windings, etc

$$E = K\dot{x} + Z_{EW} i$$

$$E = \frac{KF}{Z_m} + Z_{EW} i$$

that is

$$E = \frac{K^2 i}{Z_m} + Z_{EW} i$$

$$\therefore \quad \frac{E}{i} = \frac{K^2}{Z_m} + Z_{EW}.$$

But $\frac{E}{i}$ is the total electrical impedance Z_{ET} of the receiver

$$\therefore \quad Z_{ET} = \frac{K^2}{Z_m} + Z_{EW} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

To find out Z_m:—Let us consider the diaphragm of the receiver when it is vibrating in its fundamental mode It can be regarded as a certain equivalent mass subject to elastic restraint, and moving under the action of impressed magnetic forces

$$m\frac{d^2x}{dt^2}+r\frac{dx}{dt}+SK = F-ap$$

since

$$P = Z_1\xi a = Z_1\dot{x}a$$

$$m\ddot{x}+r\dot{x}+sx+a^2Z_1\dot{x} = F \qquad . \quad . \quad .. \quad (a)$$

where x is the deflection at the centre of the diaphragm,

m the effective mass of the diaphragm,

r the damping force per unit velocity of the diaphragm,

s the force required at the centre of the diaphragm to produce unit deflection,

a the area of cross-section of the tube,

p the excess pressure due to sound waves

$\dot{x} = e^{j\omega t}$

$\therefore$ (a) becomes

$$mj\omega\dot{x}+rx+\frac{s\dot{x}}{j\omega}+a^2Z_1\dot{x} = F$$

or

$$\frac{F}{\dot{x}} = r+j\left(m\omega-\frac{s}{\omega}\right)+a^2Z_1$$

But we know from definition that $\frac{F}{\dot{x}}$ is equal to the mechanical impedance Z_m

$$\therefore\ Z_m = r+j\left(m\omega-\frac{s}{\omega}\right)+a^2Z_1 .$$

Putting R_p for r and X_p for $\left(m\omega-\frac{s}{\omega}\right)$

$$Z_m = R_p+jX_p+a^2Z_1$$

putting this value in (1)

$$Z_{ET} = Z_{EW}+\frac{K^2}{R_p+jX_p+a^2Z_1} \qquad .. \quad .. \quad .. \quad (2)$$

In this equation R_p, X_p, and K^2 are constants for the receiver for a certain frequency and temperature.

To find Z_1:—The value of Z_1 will depend upon the length of the air column and the nature of the piston when it serves as a reflector. Consider a sound wave travelling in a pipe of uniform cross-section incident on a piston and reflected back. Assuming that the source is at the origin, the particle velocity of the incident waves is given by $\dot{\xi} = Ae^{jk(ct-x)}$, that of the reflected wave is

$\xi_r = A\alpha e^{jk(ct+x-2l)}e^{jk\beta}$ where α is the coefficient of reflection and $k\beta$ is the phase change, $k = \frac{2\pi}{\lambda}$

In the resultant wave motion the particle velocity is given by

$$\dot{\xi} = Ae^{jk(ct-x)} + A\alpha e^{jk\beta}e^{jk(ct+x-2l)}$$

and the resultant pressure is

$$p = Z_0\{Ae^{jk(ct-x)} - A\alpha e^{jk\beta}e^{jk(ct+x-2l)}$$

where Z_0 is the mechanical impedance of unit area of air column of infinite length

Hence

$$Z_1 = \frac{p}{a\xi} = \frac{Z_0}{a}\left\{\frac{1-\alpha e^{jk\beta}e^{-jk\,2l}}{1+\alpha e^{jk\beta}e^{-jk\,2l}}\right\} \text{ at } x = 0$$

$$\therefore \quad Z_1 = \frac{Z_0}{a}\left\{\frac{1-\alpha^2}{1+\alpha^2+2\alpha\cos k(2l-\beta)} + \frac{2j\alpha\sin k(2l-\beta)}{1+\alpha^2+2\alpha\cos k(2l-\beta)}\right\}$$

l represents the length of the vibrating column, the piston being situated at $x = l$

Putting this value of Z_1 in equation (2) we get

$$Z_{ET} = Z_{EW} + \frac{K^2}{R_p+jX_p+aZ_0\left\{\frac{1-\alpha^2}{D}+\frac{2j\alpha\sin\theta}{D}\right\}}$$

where

$$D = 1+\alpha^2+2\alpha\cos k(2l-\beta)$$

and

$$\theta = k(2l-\beta)$$

or

$$Z_{ET} = Z_{EW} + \frac{K^2}{R_p+aZ_0\frac{(1-\alpha^2)}{D}+j\left(X_p+aZ_0\frac{2\alpha\sin\theta}{D}\right)} \quad .. \quad (3)$$

2 In the case of a perfect reflector $\alpha = 1$ and $k\beta = \pi$

$$\therefore Z_1 = -\frac{Z_0}{a}j\cot kl.$$

Equation (3) gives $Z_{ET} = Z_{EW} + \frac{K^2}{R_p+j(X_p-aZ_0\cot kl)}$ . .. .. (3′)

Here we see that as the length l of the air column is changed $(X_p-aZ_0\cot kl)$ changes but R_p remains the same

∴ Putting $(X_p-aZ_0\cot kl) = X_p'$ we get

$$R_{EL}+jX_{EL} = \frac{K^2}{R_p+jX_p'} \quad .. \quad .. \quad .. \quad (4)$$

equating the real parts

$$R_p = \frac{K^2 R_{EL}}{R^2_{EL}+X^2_{EL}} = \text{constant}$$

or

$$R^2_{EL}+X^2_{EL} = \frac{K^2 R_{EL}}{R_p}$$

or

$$\left(R_{EL}-\frac{K^2}{2R_p}\right)^2+X^2_{EL} = \frac{K^2}{2R_p} \tag{5}$$

which is the equation of a circle, when R_{EL} and X_{EL} are plotted as ordinate and abscissa Thus we find that the locus of Z_{EL} is a circle of radius $\frac{K^2}{2R_p}$, tangent to the X-axis at the origin

Determination of K^2, R_p and X_p —From (3′) we get

$$\begin{aligned} R_{EL} &= \frac{K^2}{R_p^2+(X_p-aZ_0 \cot kl)^2} \\ X_{EL} &= -\frac{K^2(X_p-aZ_0 \cot kl)}{R_p^2+(X_p-aZ_0 \cot kl)^2}\,. \end{aligned} \tag{3a}$$

Put $Z_{EW} = R_{EW} + jX_{EW}$ so that R_{EW} and X_{EW} represents the electrical resistance and the reactance of the winding, etc Let ABC be the locus of Z_{EL} (Fig 1) when the perfect reflector acts as a piston From (3′) we note that

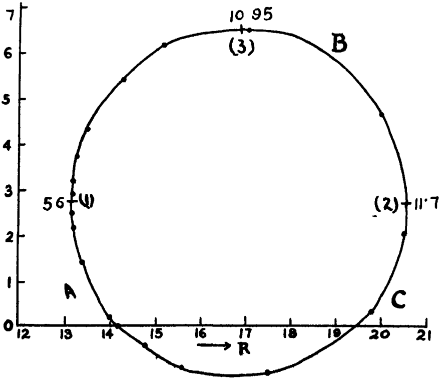

FIG 1. Impedance Circle for Perfect Reflector

when $\cot kl = \infty$ the second term vanishes, and

$$Z_{ET} = R_{EW} + jX_{EW}$$

Hence R_{EL} will be minimum and its value will be equal to R_{EW}.

At this position of the piston the reactance will be the same as X_{EW}. This point is represented on the circle as the point number (1) Again from (3a) we find when $\cot kl = \frac{X_p}{aZ_0}$; R_{EL} is maximum and $X_{EL} = X_{EW}$. This is shown by the point number (2) At point (3) $R_{EL} = X_{EL}$ measured from the point (1) as origin

Now the point (1) gives R_{EW} and X_{EW} At point (2) $X_{EL_2} = 0$ with respect to X_{EW} and

$$X_p = aZ_0 \cot kl_2 \quad \ldots \quad . \quad . \qquad (a)$$

At (3) when

$$R_{EL_3} = X_{EL_3},$$

$$R_p = -(X_p - aZ_0 \cot kl_3) \quad \ldots \quad \ldots \quad \ldots \qquad (b)$$

The radius of the circle is equal to $\frac{K^2}{2R_p}$

$$\therefore\ R_{EL_3} = \frac{K^2}{2R_p} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad (c)$$

with the help of equations (a), (b), (c); X_p, R_p and K^2 the constants of the receiver can be calculated at a constant frequency and temperature.

4. *Absorbing material.*

When instead of a perfect reflector the piston is made of some absorbing material

$Z_{ET} - Z_{EW} =$

$$\frac{K^2}{R_p + \dfrac{aZ_0(1-\alpha^2)}{1+\alpha^2+2\alpha\left(1-2\sin^2\dfrac{\theta}{2}\right)} + j\left(X_p + aZ_0\dfrac{2\alpha\sin\theta}{1\alpha+2\alpha\left(1-2\sin^2\dfrac{\theta}{2}\right)}\right)}$$

where $\theta = (2l-B)k$

$$\text{or}\quad Z_{EL} = \frac{K^2}{R_p + aZ_0\dfrac{1-\alpha^2}{(1+\alpha)^2-4\alpha\sin^2\dfrac{\theta}{2}} + j\left\{X_p + aZ_0\dfrac{2\alpha\sin\theta}{(1+\alpha)^2-4\alpha\sin^2\dfrac{\theta}{2}}\right\}}$$

$$Z_{EL} = \frac{K^2}{R_p + aZ_0\dfrac{1-\alpha^2}{(1+\alpha)^2-4\alpha\sin^2\dfrac{\theta}{2}} + j\left(X_p + aZ_0\dfrac{2\alpha\sin\theta}{D}\right)} \quad \ldots \quad \ldots \qquad (6)$$

$$D=(1+\alpha^2)\left(1-\frac{4\alpha}{1+\alpha^2}\sin^2\frac{\theta}{2}\right)$$

or $$Z_{EL}=\frac{K^2}{R_p'+jX_p'}$$

or $$R_{EL}+jX_{EL}=\frac{K^2}{R_p'+jX_p'}$$

Now if this equation be treated as equation (4) we get

$$\left(R_{EL}-\frac{K^2}{2R_p'}\right)^2+X_{EL}^2=\frac{K^2}{2R_p'}$$

here R_p' is not a constant as in the case of the perfect reflector, here

$$R_p'=R_p+\frac{1-\alpha}{1+\alpha}aZ_0\left(1+\frac{4\alpha}{(1+\alpha)^2}\sin^2\frac{\theta}{2}\right)$$

which varies as $\theta=k(2l-\beta)$ changes; so we see that in the case of an absorbing material locus of Z_{EL} will not be a perfect circle but a curve of changing radius and shifting centre

5. *Determination of* α:—If $\sin^2\frac{\theta}{2}$ be neglected as it is very small, from (6) we get

$$Z_{EL}=\frac{K^2}{\left\{R_p+aZ_0\frac{1-\alpha^2}{(1+\alpha)^2}\right\}+j\left\{X_p+\frac{2\alpha\sin\theta}{(1+\alpha)^2}\right\}}$$

$$Z_{EL}=\frac{K^2}{\left\{R_p+aZ_0\frac{1-\alpha}{1+\alpha}\right\}+j\left\{X_p+\frac{2\alpha\sin\theta}{(1+\alpha)^2}\right\}} \quad . \qquad (7)$$

which is again an equation of a circle. In the case of an absorber also the shift is so small that for all practical purposes we can consider it a circle. Then the radius of this circle is given by

$$\frac{K^2}{2R_p'}=\frac{K^2}{2\left(R_p+\frac{1-\alpha}{1+\alpha}aZ_0\right)}\text{ (approx.)}$$

$$\therefore \text{ Radius}=\frac{K^2}{2\left(R_p+\frac{1-\alpha}{1+\alpha}aZ_0\right)} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (8)$$

Knowing R_p and K^2 from the case of the perfect reflector α can be calculated if the radius be known.

6 *Determination of Phase change*

In the case of an absorbing material also when R_{EL} is maximum X_{EL} is zero approximately, hence from equation (7)

$$X_p+\frac{2\alpha\sin\theta}{(1+\alpha)^2}=0$$

$$\text{or }\sin\theta=-\frac{X_p(1+\alpha)^2}{2\alpha}.$$

This holds good only if $(1+X_p^2)$ is negligible, otherwise

$$\sin\theta=\frac{-X_p(1+\alpha)^2}{2\alpha(1+X_p^2)}$$

$$\sin\theta=\sin(2l-\beta)k=-\frac{X_p(1+\alpha)^2}{2\alpha(1+X_p^2)} \qquad (9)$$

knowing X_p from the case of the perfect reflector and α from (8), $k\beta$ can be calculated if l be known l is the equivalent length of the air column from the origin to the point where R_{EL} is maximum

PART II

1 *Experimental details* .—

To find out Z_{EL}, the electrical impedance of the receiver, a cylindrical brass socket S was fitted to the mouth of the receiver To this socket was attached a brass tube AB A snugly fitting brass piston, having two piston rings, formed the termination of this tube As this type of piston formed a very efficient seal, it was necessary to have a pressure hole H in the brass socket S which could be opened or closed by a brass screw In order to avoid tearing of the diaphragm by change in air pressure, the hole was always opened before moving the piston to and fro A pointer attached to the piston rod R moves on a scale and measures the shift of the piston and thus the length of the air column

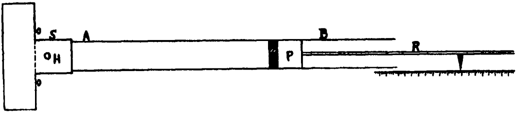

FIG 2

The source of sound was a beat frequency oscillator To prevent overloading of the receiver with its consequent distortioning effect, as low an input level was used, as was consistent with the method of measurement

The oscillating body was the diaphragm of a moving coil electro-magnet type of receiver Before making the measurements the receiver was allowed to reach thermal equilibrium with its field excited as both the field excitation and the mechanical properties of a diaphragm are functions of temperature

When the receiver worked, it filled the tube with sound As the piston was moved, the length of the air column changed, thus the electrical impedance of the receiver also changed in the manner indicated by equation (3) of the first part The electrical impedance is the sum of resistance and reactance It was found that the reactance had positive as well as negative values depending upon the length of the air column and the nature of the reflecting piston

To measure this reactance and resistance, we first tried Anderson's bridge, but it was found incapable of measuring negative reactances It could not also detect very small changes of resistance and reactance So in the end we used Campbell's inductometer It proved quite sensitive and accurate for measuring both positive and negative inductances of the order of one microhenry For resistance measurement a dial resistance box reading up to 0 1 ohms accurately was used Large errors can arise in effective resistance measurements, on account of (1) the small residual reactance of the ratio arms, and (2) the earth capacitance From the theory[4] we see that when the ratio arms have equal resistances and residuals no errors arise in the measurements With unequal ratio arms, but with their residuals in the same ratio as their resistance, errors due to residual effects are also entirely eliminated In the present case the resistance of the ratio arms when measured separately was found equal Also whether the residuals were equal or not was checked by balancing the bridge and then interchanging the ratios, it was found that by interchanging, the balance was not upset That showed that the residuals were also equal Hence we conclude that no errors due to residuals were introduced in the resistance measurements There was a difference of 07 ohms in the resistance of primaries, which did not interfere with the resistance measurements to any appreciable extent

To avoid earth capacitance effect, shielded wires were used for connections, with their shields connected to earth and the inductometer was insulated and kept at a distance from the oscillator Wagner's earthing device was also tried but it did not make any appreciable improvement

The arrangement of the apparatus is shown in fig 3 To avoid using the negative scale of the inductometer, a small known inductance L was put in series with the unknown impedance In series with L was put a thermo-milli-ammeter to keep the input current constant as it changes with the change of air load impedance. The current is adjusted by the volume control knob of the beat frequency oscillator A low resistance telephone was used to detect small changes of impedance in the circuit

To find out the resistance and the reactance terms of an impedance, both resistance and inductance were adjusted till there was minimum sound in the telephone. The sound never vanished. Even Wagner's earthing device could not improve this minimum Perfect silence could not be obtained due to the presence of harmonic content in the oscillator.

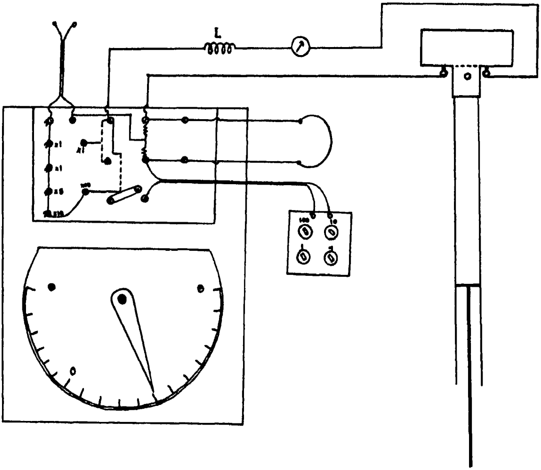

FIG. 3.

2 *Observations and Calculations*

After making all the arrangements as described before, the oscillator and the field magnet current were switched on. The maximum current for the magnet is 1·6 amperes, but for our purpose 1·2 amperes were enough. This 1·2 amperes current was maintained constant with the help of a slide resistance throughout the experiment. The oscillator was adjusted for a frequency of nearly 1,200 cycles. To maintain this frequency constant, it was very necessary that the temperature of the oscillator should remain constant. For that purpose a fan was put on and this kept the temperature satisfactorily constant. The exact frequency was calculated from the observed half wave-length in terms of the length of the air column between two nodes or antinodes. At first, resistance and inductance were adjusted to find the balance keeping the receiver out of circuit. This gave us the initial resistance and inductance of the circuit which was subtracted from every reading. The difference gave the total impedance of the circuit. Then the piston was pushed *into its extreme inward position*, and balance was found by adjusting the resistance and inductance and this position of the piston was read as the zero of the scale.

Then the piston was pushed out a little, again resistance and inductance were adjusted to get a balance and the position of the piston noted. In this manner the readings were taken at small distances, until after moving the piston through a length equal to half wave-length they began to repeat themselves. This gave us the electrical resistance and inductance corresponding to the acoustical impedance of the known length of air column. Inductance in each case was then multiplied by $2\pi f$ to get the reactance, f denoting the frequency of sound. A curve was drawn between resistance as abscissa and reactance as ordinate, which was found to be a circle in accordance with equation (5).

Then three points were taken on this circle: (i) where resistance R_{EL} is minimum, (ii) R_{EL} is maximum, and (iii) R_{EL} is equal to X_{EL}. Then according to equations (a), (b) and (c), the constants K^2, R_p, and X_p of the receiver were calculated for the particular frequency and temperature. A typical case is given below:—

Temperature = 26·5°C
Field magnet current = 1·2 amperes.
Initial resistance = 9 4 ohms.
Initial inductance reading = 3 2

The readings below are given after subtracting the initial resistance and inductance readings.

Scale Reading l.	Resistance R	Inductance reading L.	Reactance $1{\cdot}538L$ X.
0	14·05	·1	·154
2	13·4	·9	1·384
4	13 2	1·4	2·15
5	13·2	1·6	2·46
6	13·2	1·85	2·84
7	13·2	2·05	3·15
8	13·3	2·4	3·69
9	13·5	2·8	4 3
10	14·3	3·5	5·38
10·5	15·2	4·0	6·15
11	17·1	4·2	6·45
11·5	20·0	3·0	4·6
11·8	20·5	1·3	2·0
12·0	19·8	·2	·308
12·5	17·5	—·7	—1·07
13	15·6	— 6	—·923
13·5	14·8	—·3	—·46
14	14·15	·05	·077
14·2	14·05	·1	·154

½ wave-length = 14·2 cm

∴ wave-length $\lambda = 28{\cdot}4$ cm

Velocity of sound $331\ 3 + 61t$

where t is the temperature

∴ Velocity $V = 331\ 3 + 61 \times 26\ 5$

$= 347{\cdot}46$ meters

∴ Frequency $\frac{347\ 46}{28{\cdot}4} \times 100 = 1223\ 4$ cycles

∴ $2\pi f = 2 \times 3\ 142 \times 1223\ 4 = 7695$

Now reactance is equal to $2\pi f$ times inductance If L' denotes inductance and X reactance, $X = 2\pi f L'$

But $L' = 2 \times 100 \times L$

because L is the inductometer scale reading which is always multiplied by 2 and the multiplying factor used, which in this case was 100

∴ Reactance $X = 400\pi f L = 1\ 54 \times 10^6 L$ Microhenries

$= 1\ 54L$ Henries

After calculating X in every case a curve was drawn between resistance and reactance and three points taken as described in § 3, Part I, and length readings noted at these points

If l denotes the length reading at point (l)

$$l = 5{\cdot}6 \text{ cm}$$

According to theory the point where the resistance R_{EL} is minimum should be at a distance $\frac{\lambda}{2}$ from the origin, therefore effective length l' of the air column from our zero of the scale to the origin is given by

$$l' = \frac{\lambda}{2} - l = 14\ 2 - 5\ 6 = 8{\cdot}6 \text{ cm}$$

∴ $l' = 8{\cdot}6$ cm should be added to every length reading to get the real length of the air column Thus

at point (2) $l_2 = 11\ 7 + 8\ 6 = 20{\cdot}3$ cm.

„ „ (3) $l_3 = 10{\cdot}95 + 8\ 6 = 19{\cdot}55$ cm

$R_{EW} = 13{\cdot}2$ ohms

$R_{EL_2} = 20{\cdot}5 - 13{\cdot}2 = 7\ 2$ ohms

$R_{EL_3} = 16\ 85 - 13\ 2 = 3{\cdot}65$ ohms

From equation (a)

$$X_p = aZ_0 \cot \frac{2\pi}{\lambda} l_2$$

$$= aZ_0 \cot \frac{360}{28{\cdot}4} \times 20\ 3$$

$$= {\cdot}22\ aZ_0.$$

From equation (b)

$$R_p+X_p = aZ_0 \cot \frac{360}{28\ 4} \times 19\ 55$$

From equation (c)

$$\frac{K^2}{2R_p} = R_{EL_3} = 3\ 65$$

or

$$\begin{aligned} K^2 &= 2\times{\cdot}186\times 3\ 65\ aZ_0 \\ &= 1\ 36\ aZ_0 \\ R_p &= 0\ 19\ aZ_0 \\ X_p &= 0\ 22\ aZ_0 \\ K^2 &= 1\ 36\ aZ_0 \end{aligned}$$

Absorbing material

After knowing the constants of the receiver in this way, the absorbing material was put at the piston and the piston was *pushed into its extreme position* Then the experiment was repeated in the same way, keeping all the other conditions the same as in the case of the reflector The following were the observations when cotton was used as an absorber

For cotton fig 4

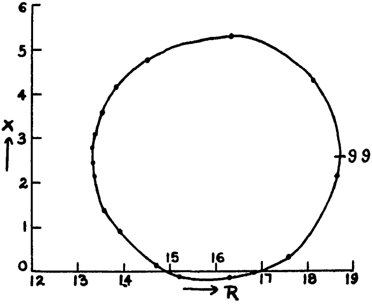

FIG. 4. Impedance Curve for Cotton.

Scale Reading l	Resistance R.	Inductance Reading L.	Reactance $X = 1{\cdot}538L$
0	13 6	·9	1·38
2	13·35	1·4	2·15
3	13·3	1·6	2 46
4	13 3	1·8	2 77
5	13·35	2·0	3·08
6	13 5	2 3	3·54
7	13·8	2·7	4·15
8	14 5	3 1	4·75
9	16·3	3 5	5·38
9·5	18·1	2·8	4·3
10	18·6	1·4	2·15
10 5	17 6	0·2	31
11·0	16·3	−·1	−·15
11·5	15·2	−·1	−·15
12·0	14 7	+·1	·15
13 0	13·9	·6	92
14·0	13 6	·9	1·38

A graph was drawn between resistance and reactance and the length was noted at the point where the resistance was maximum Reactance at this point was nearly the same as X_{EW}, the reactance of the windings, etc. The difference of this resistance and R_{EW} gave us R_{EL} and the length when added to effective length gave the length of the air column

At the point of maximum resistance

$$l = 9{\cdot}9+8\ 6 = 18\ 5 \text{ cms}$$

$$R_{EL} = 18\ 7-13\ 2 = 5{\cdot}5 \text{ ohms}$$

From § 5 equation (8)

$$\frac{K^2}{2\times\text{Radius}} = R_p+\frac{1-\alpha}{1+\alpha}aZ_0$$

or

$$\frac{K^2}{R_{EL}} - R_p = \frac{1-\alpha}{1+\alpha}aZ_0$$

Putting the values of K^2, R_p and R_{EL}

$$\frac{1-\alpha}{1+\alpha} = \frac{1\ 36}{5\ 5} - 19$$

$$= 25 - 19 = 016$$

$$\alpha = \frac{939}{1\ 061} = 885$$

Absorption coefficient $= 1-\alpha^2 = 1{\cdot}78 = 22$

From § 6 equation (9)

$$\sin\frac{2\pi}{\lambda}(2l-\beta) = -\frac{X_p(1+\alpha)^2}{2\alpha(1+X_p^2)}$$

or putting the values of X_p and α

$$\sin\frac{2\pi}{\lambda}(2l-\beta) = -\frac{22\times 1\ 885^2}{1\ 77\times 1\ 05} = -\ 42$$

$$\therefore\ \frac{2\pi}{\lambda}(2l-\beta) = -25^\circ\ 1$$

Putting the value of l

$$\frac{2\pi}{\lambda}\beta = \frac{360\times 37}{28\ 4}+25\ 1 = 494\ 1$$

$$\therefore\ k\beta = 494\ 1-360 = 134^\circ\ 1$$

reflection coefficient α = ·885
absorption coefficient = 22
phase change = 134°·1

In this way observations were taken for every material and absorption coefficient, reflection coefficient and phase change calculated in every case separately

The following table gives the data for some substances.—

	Substance	Reflection coefficient	Absorption coefficient	Phase change
1	Asbestos ..	·96	·085	175°·1
2	Cotton	·88	·22	134°·1
3	Insulating board	·83	·30	172°·3
4.	Treetax	81	35	175°·5
5	Felt . .	81	35	145°·5

The impedance circles are as shown for these materials. A glance at these circles (Figs. 5, 6, 7, 8) shows whether the substance has got a greater

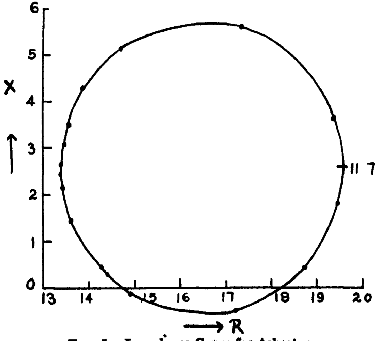

FIG. 5. Impedance Curve for Asbestos.

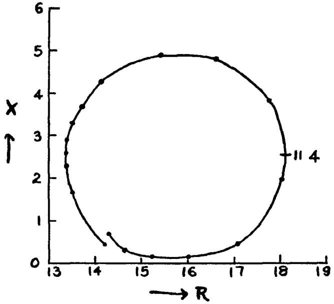

FIG 6 Impedance Curve for Insulating board

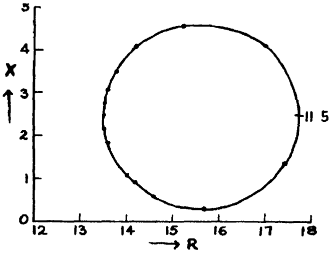

FIG 7 Impedance Curve for Felt

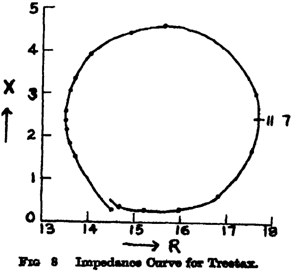

FIG 8 Impedance Curve for Treetax.

absorption coefficient from the former one or smaller. Theoretically also we see from equation (8) that radius

$$= \frac{K^2}{2\left(R_p + \frac{1-\alpha}{1+\alpha} a Z_0\right)}$$

If the radius becomes smaller, $R_p + \frac{1-\alpha}{1+\alpha} a Z_0$ should increase R_p is constant $\frac{1-\alpha}{1+\alpha} a Z_0$ must increase, i e α must decrease, so absorption increases Hence as the absorption coefficient increases the circle becomes smaller From the above table we see that there is no relation between absorption coefficient and phase It is possible that the coefficients may remain the same while the phase changes in two cases as can be noted in cases (4) and (5), or the phase remains the same and coefficients alter as found in (1) and (4) The discussion in part III will show that phase change depends on the perforated area of the reflecting surface in comparison to the solid one When the perforated area is more the phase change increases Evidently, the observations show that felt is more porous than treetax, and though the coefficients of reflection and absorption are much different for asbestos and treetax, yet the perforated area is the same

Cotton shows a peculiar case here Absorption is only twenty per cent, and phase change is so large This requires further investigation

PART III

Theory of Sound absorption in porous materials

The theory of absorption and reflection of sound was first treated theoretically by Rayleigh[5] and elaborated by Paris[6] They treated the case of sound incident normally on a wall consisting of a large number of similar conduits of circular cross-section and uniformly distributed The expressions deduced by them give the ratio of the amplitudes of the incident and reflected waves

Two cases arise according to whether the tubes are narrow or of moderate bore. It is known[7] that the criterion which separates the two cases is the quantity $r\left(\frac{j\omega}{\nu}\right)^{\frac{1}{2}}$ in which r is the radius of the capillary, ν is the kinematic viscosity of air, ω is the cycle frequency $2\pi f$ If this expression is less than unity, the tube, according to Rayleigh, is effectively 'narrow' If it lies between 1 and 10, it is of moderate bore. The equation for the sound waves passing through a narrow tube is

$$\xi = \xi_0 e^{-px} e^{j(\omega t - qx)} .$$

Case 1. When the tube is narrow

$$p = q = 2\ 82\beta \quad \text{where} \quad \beta = \frac{1}{rc}\sqrt{\frac{\omega\nu}{2}}$$

Case 2. When the tube is of moderate bore

$$p = \beta$$

$$q = \frac{\omega}{c} + \beta$$

The acoustic impedance $Z_0 = \rho c$ of a gaseous medium characterizes its behaviour with regard to waves passing through it In the case of a capillary tube of infinite length, the acoustic impedance Z' *per unit area* can be calculated as follows.—

Since $$p = -c^2\rho\frac{d\xi}{dx} \quad \text{and} \quad \xi = \frac{\xi}{j\omega}$$

and $$Z' = \frac{p}{\xi}$$

we obtain at once Case I·

$$Z' = Z_0(1-j)\left(\frac{4\nu}{\omega r^2}\right)^{\frac{1}{2}}$$

Case II

$$Z' = Z_0\left\{1+(1-j)\left(_{2\omega r^2}\right)^{\frac{1}{2}}\right\}$$

If the tube, however, is of finite length l, we must replace these equations by others involving the impedance of a finite pipe which is [8]

$$Z_l = -jZ \cot l(q-jp)$$

The impedance factor given above must then be multiplied by—

Case I

$$\cot\{\sqrt{8}(1-j)l\beta\}$$

Case II

$$\cot\left\{\frac{\omega}{c}+\beta l(1-j)\right\}$$

to obtain the appropriate value of the relative impedances

If the waves are incident from a medium of impedance Z_0 to another of impedance Z_2 then the reflection coefficient is given by [9]

$$e^{jk\beta\alpha} = -\frac{\frac{Z_2}{Z_0}-1}{\frac{Z_2}{Z_0}+1}$$

In the present experiment we wanted to find out the absorption and reflection coefficients for known numbers of glass tubes and their corresponding phase change. For this purpose a number of holes were bored in the piston and filled with glass tubes In this case a part of the sound waves was reflected from the porous material and a part was reflected from the solid surface If A denote the perforated area we have $\xi_1+\xi_r=\xi_2 A$ where ξ is the reflected wave both from the solid and perforated parts, ξ_1 is the incident wave

$$\xi_r = \dot{\xi}_r{}' + \xi_r{}''$$

$$\xi_1 + \dot{\xi}_r = \dot{\xi}_2 A$$

$$p_1 + p_r = p_2 \text{ where } p \text{ is the excess pressure}$$

$$\xi_1 - \xi_r = \frac{Z_2}{Z_0}\xi_2$$

Z_2 being the impedance of the opening

$$Z_0 = Z_2 = c\rho$$

Thus

$$\frac{\xi_r}{\xi_1} = \frac{A - \dfrac{Z_2}{Z_0}}{A + \dfrac{Z_2}{Z_0}}$$

This can be written in the form

$$\alpha e^{jk\beta} = -\frac{\dfrac{Z_2}{Z_0} - A}{\dfrac{Z_2}{Z_0} + A} \qquad . \qquad . \qquad (10)$$

where $k\beta$ denotes the change of phase

The experiment was repeated in the same way as described for other absorbing materials in § 2, Part II. For different numbers of tubes the coefficients and phase changes were calculated In this case also the impedance circles

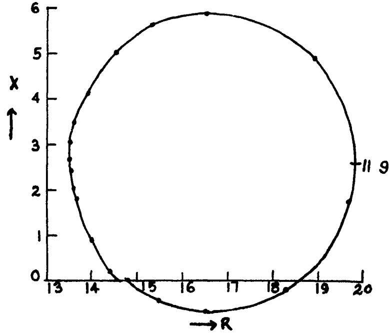

FIG. 9 Impedance Curve for 25 Capillary tubes.

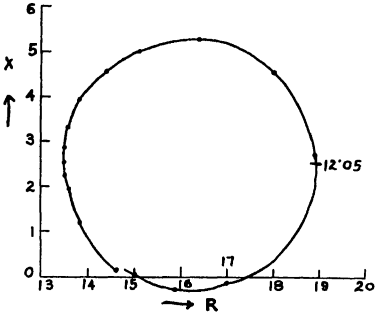

FIG 10 Impedance Curve for 50 Capillary tubes.

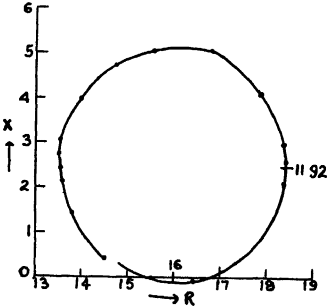

FIG. 11. Impedance Curve for 75 Capillary tubes.

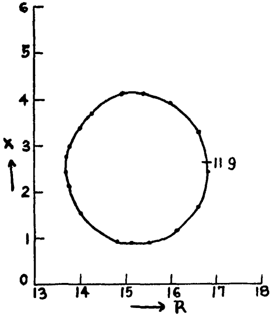

FIG 12 Impedance Curve for 100 Capillary tubes

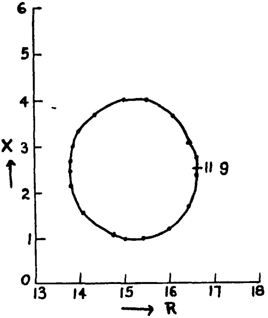

FIG 13 Impedance Curve for 125 Capillary tubes

became smaller and smaller as the number of tubes increased, showing thereby that the absorption was increased The following table gives the results obtained.—

Number of tubes	A	Reflection coefficient	$\frac{Z_2}{Z_0}$	Absorption coefficient	Phase change $k\beta$
125	·078	·64	·355	·59	185·5
100	·064	·67	·324	·55	185·1
75	·048	86	638	·26	184·5
50	·032	89	55	21	184 0
25	·016	·96	78	08	183·7

It is found that the absorption coefficient increases with the number of tubes, but there is no appreciable change in phase The phase change is nearly the same in every case The phase change depends on the perforated area A, as can be shown from equation (10) If A be very small, nearing zero, then at $A = 0$

$$\alpha = +\frac{\left(\frac{Z_2}{Z_0}-0\right)}{\left(\frac{Z_2}{Z_0}+0\right)} = +1$$

which is the case of perfect reflector for which phase change is 180°

In the present case of glass tubes the radius of a tube is ·05 cm. and if 125 tubes are taken the perforated area of the tubes

$$= \pi r^2 n = 3{\cdot}14 \times {\cdot}05^2 \times 125$$

The area of the piston is $\pi R^2 = 3\ 142 \times 2^2$, as $R = 2$ cm

$$\therefore\ A = \frac{\pi r^2 n}{\pi R^2} = \frac{125 \times 05^2}{4} = 078$$

$$A = {\cdot}078 \text{ is very nearly zero}$$

As shown before

$$\frac{Z_2}{Z_0} = \left(\frac{4\nu}{\omega r^2}\right)^{\frac{1}{2}} (1 - \jmath)$$

Leaving aside the imaginary part

$$\frac{Z_2}{Z_0} = \sqrt{\frac{4\nu}{\omega r^2}}$$

$$\frac{Z_2}{Z_0} = \frac{2}{r}\sqrt{\frac{\nu}{2\pi f}} = \frac{2}{05}\sqrt{\frac{132}{2 \times 3\ 142 \times 1200}}$$

$$= 0\ 2$$

As ν the kinematic viscosity is affected by conductivity, etc., in this case it almost becomes four times 132 so the value of

$$\frac{Z_2}{Z_0} \text{ becomes } \frac{Z_2}{Z_0} = 2 \times 2 = 4 \text{ approximately}$$

Experimentally, we find that according to equation

$$e^{\jmath k\beta}\alpha = -\frac{\frac{Z_2}{Z_0} - A}{\frac{Z_2}{Z_0} + A} \quad \text{or} \quad \frac{Z_2}{Z_0} = \frac{A(1 - \alpha e^{\jmath k\beta})}{(1 + e^{\jmath k\beta}\alpha)}$$

putting the value of A for the number of tubes used and α obtained from experimental observation, we get the value of $\frac{Z_2}{Z_0}$ The value of $\frac{Z_2}{Z_0}$ for each case is given in the table It is found that the order of the result is the same as found theoretically.

As the area A has a maximum value equal to ·078 it is evident that there will be a very small difference between the phase change in this case and that for a perfect reflector We see that phase change varies from 183 to 185 only, but in every case it does exceed 180° Why it is more than 180° in this case of tubes and not less than 180° as in the case of felt, treetax, etc., requires further investigation

Acknowledgements.

It is a pleasure to express my sincere thanks to Prof. S. R. Bhargava for his interest in this work and to Dr R N Ghosh for suggesting the problem and his continuous guidance

Abstract.—The absorption coefficient of sound has been investigated for a large number of porous substances, but the phase change accompanying

reflection had not been so far investigated This is done in the present paper by measuring the impedance of a telephone receiver in the presence of air load. No significant relation between absorption coefficient and phase change has been found The phase change in the case of porous materials made from assembling capillary tubes is found to be greater than π at the frequency of 1200 cycles whereas in other substances it was less than π The acoustic impedance of the capillary tubes as calculated from Rayleigh's formula is found to be in reasonable agreement with experiment

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MALE AND FEMALE GAMETOPHYTES OF *POLEMONIUM COERULEUM* LINN., WITH A DISCUSSION ON THE AFFINITIES OF THE FAMILY POLEMONIACEAE

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(Communicated by Dr A C Joshi, D Sc)

(*Read August 20, 1940*)

Polemoniaceae is a comparatively small family with 12 genera and about 300 species, distributed chiefly in N America A few species, however, extend to Chili, Peru, Europe and N Asia The family is generally included among the Tubiflorae, one of the orders of the Gamopetalae, but there is a great deal of difference of opinion about its ancestry among the Polypetalae The few previous observations on the embryo-sac are conflicting The embryo-sac development in *Gilia millefoliata* and *Cobaea scandens* is said to follow the *Normal*-type, while in *Polemonium coeruleum* it has been described to follow the *Scilla*-type (Schnarf, 1931) Such a situation is unusual and requires reinvestigation.

Polemonium coeruleum Linn, the Jacob's ladder, is one of the most widely distributed members of the family, being spread over North and Central Asia, Europe and N America Its distribution is coextensive with that of the family It is found in India in the alpine Western Himalayas, from Kumaon to Kashmir, at a height of 9,000–12,000 ft It is quite common in this area The plant is a perennial herb with alternate, pinnate leaves and fine blue showy flowers arranged in terminal corymbose cymes The present paper deals with the development and structure of the anther, pollen, ovule and embryo-sac of this species In the end the bearing of the embryological characters on the affinities of the family Polemoniaceae is discussed.

The material of *Polemonium coeruleum* used in the present investigation was collected by Dr. A C Joshi from Khilanmarg (10,000–11,000 ft.) in the Kashmir State It was fixed in Navashin's fixative and then transferred directly to 70% alcohol Afterwards customary methods of dehydration and embedding were followed Sections were cut 8–12 μ thick and stained with Delafield's and Heidenhain's iron-alum haematoxylin With the latter stain, counterstaining with light green was also tried on some slides

PREVIOUS WORK.

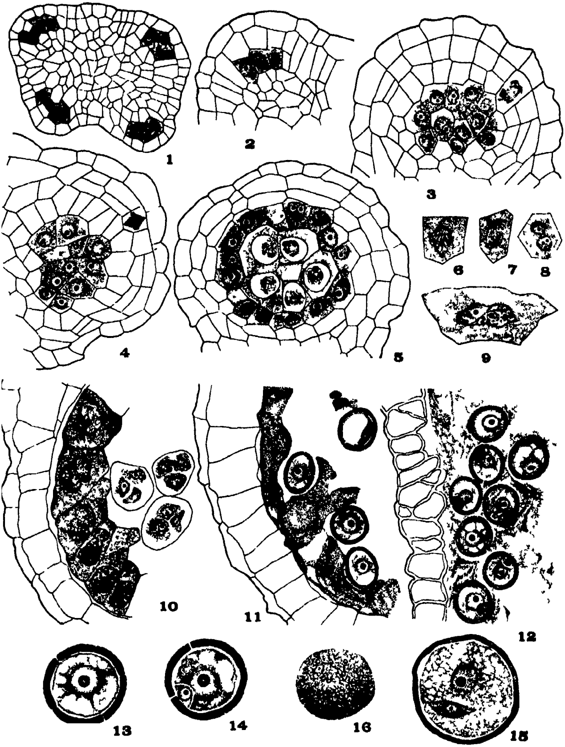
The earliest embryological observations on the family Polemoniaceae were made by Elfving (1879) and Jönsson (1879-80). Elfving in his work

VOL. VI—No. 4. [Published December 10th, 1940.

on the pollen grains of angiosperms also studied the pollen of *Gilia* species. Jönsson studied the development of the embryo-sac of *Polemonium coeruleum*. According to him it follows the *Scilla*-type Billings (1901) studied the structure of the ovule and embryo-sac, though not all the developmental stages, of three species of *Polemonium*, *Collomia coccinea*, *Phlox Drummondi*, *Leptosiphon Androsoce* and *Gilia millefoliata* He noted in all species unitegmic ovules, embryo-sac tapetum, 8-nucleate embryo-sac, early degenerating antipodals and nuclear endosperm. Bonnet (1912) in his work on the tapetum of angiosperms also reported on the tapetal cells of *Cobaea scandens*, noting the periplasmodium formation Juel (1915) made a similar study both of *Cobaea* and *Polemonium* He noted amoeboid periplasmodium in the first, but not in the second Farr (1920) studied cytokinesis in the pollen-mother cells of *Cobaea scandens* He found this to take place according to the simultaneous method and furrowing Schnarf (1921) showed the development of the embryo-sac in *Gilia millefoliata* to follow the *Normal*-type Dahlgren (1927) has figured the structure of the nucellus of *Cobaea scandens* Schurhoff (1926) and Schnarf (1937) have summarized the earlier work on the family Schnarf (1937) reports 2-nucleate mature pollen grains in *Gilia* and *Phlox* species

MICROSPOROGENESIS

Even before the young anther has become distinctly 4-lobed, 3–4 rows of cells in each lobe assume a different appearance from the rest These cells begin to stain more deeply than the rest and show a higher nucleus to cytoplasm ratio, and thus differentiate as the primary archesporium (Fig 1) Each of these primary archesporial cells, after the anther has become distinctly 4-lobed, cuts off a primary wall cell towards the outside (Fig 2) Divisions now proceed rapidly both in the primary wall cells and primary sporogenous cells and the anther soon attains its mature form The primary wall cells divide periclinally forming two layers (Fig. 3). The inner one of these layers develops directly into the tapetum, while the cells of the outer layer undergo one more periclinal division (Fig. 4) The anther wall thus becomes four layers thick including the epidermis (Fig 5). The layer of cells just below the epidermis persists throughout the development of the anther and by the development of the special thickenings differentiates as the fibrous endothecium (Figs 10–12) The middle layer of cells situated in between the tapetal and fibrous endothecial layers is short-lived. As the other two layers develop, it is crushed by the growing pressure from both inside and outside. Such a differentiation of the anther wall agrees with that found in *Ranunculus sceleratus* by Singh (1936), with the only difference that in *Ranunculus sceleratus* there are two middle layers Other species of the same genus, however, show only one middle layer, e.g, *Ranunculus parviflorus* studied by Salisbury (1931). Similar development of the anther wall is also seen in the Labiatae (Guérin, 1919), Valerianaceae (Asplund, 1920), etc. In the Caryophyllaceae and other



FIGS. 1–16 *Polemonium coeruleum*. Various stages in the development of the anther and pollen. Fig. 1, T S of a young anther showing 3-4 rows of primary archesporial cells in each lobe. Figs 2–5, four stages in the development of the parietal tissue. Figs. 6–9, four stages in the development of tapetal cells. Fig. 10, part of an anther-lobe showing much enlarged tapetal cells, fusion of the tapetal nuclei and pollen tetrads Fig. 11, an early stage in the development of false periplasmodium with degenerating tapetal nuclei and 1-nucleate pollen grains Fig. 12, false periplasmodium fully developed, pollen grains 2-celled and fibrous endothecial layer completely differentiated. Fig. 13, 1-nucleate pollen grain. Fig. 14, a young 2-celled pollen grain. Fig. 15, mature pollen grain. Fig. 16, surface view of a mature pollen grain. Figs. 1 and 11-12, × ca. 266; Figs. 2-5 and 10, × ca. 466; Figs. 6–9 and 13-16, × ca. 533.

families of Centrospermales, with which the affinity of the Polemoniaceae has been suggested by several persons (see discussion), the development of the parietal tissue in the anther follows a slightly different course We find both in Caryophyllaceae (Joshi, P C, 1935) and Amarantaceae (Kajale, 1936), Chenopodiaceae (Bhargava, 1936), Phytolaccaceae (Joshi, 1936), Nyctaginaceae (Bhargava, 1930), etc, that the cells of the outer layer formed by the first division of the primary wall layer do not divide any further periclinally and the inner layer does not develop directly into the tapetum Its cells undergo at least one more division before the differentiation of the tapetum from the innermost layer Unfortunately, we have no similar authentic work to compare among any of the Geraniales, the second order from which this family is supposed to have been derived by many taxonomists

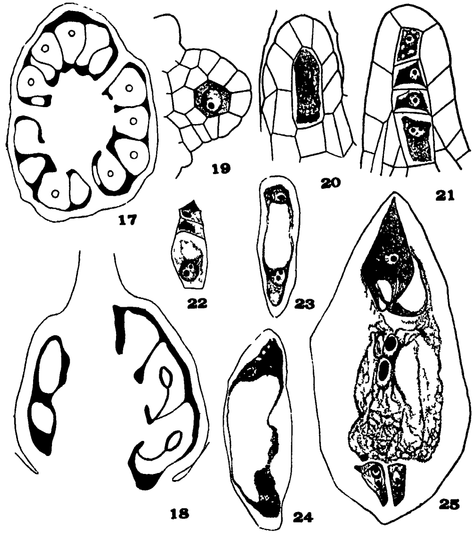
During the early prophase of the first meiotic division in the pollen-mother cells, the nuclei of the tapetal cells are still in the resting condition (Fig 5) Usually among the flowering plants they divide about the zygotene stage In *Polemonium coeruleum* they were found to divide in a mitotic manner (Figs 6 and 7) only when the nuclei of the pollen-mother cells entered the diplotene stage The cells remain 2-nucleate for some time (Fig 8), but by the time of cytokinesis in the pollen-mother cells the nuclei come together and fuse with each other (Figs 9 and 10), so that the tapetal cells become 1-nucleate once again This condition, however, differs from the first uni-nucleate stage in the fact that the single nucleus now is tetraploid Similar division of the tapetal nuclei and fusion of the daughter nuclei to form polyploid nuclei is seen in many other flowering plants, e g, *Galtonia candicans* (Smith, 1933), *Wickstroemia indica* (Winkler, 1906), *Gynandropsis pentaphylla* (Raghavan, 1938), *Polianthes tuberosa* (Joshi and Pantulu, unpublished observations), etc Cooper (1933) reports that in *Phlox paniculata* the tapetal cells are generally uni-nucleate, but occasionally they become 2-nucleate during the late prophase or metaphase of the I meiotic division in pollen-mother cells. This would show that there is considerable difference in the behaviour of tapetal cells within the family Polemoniaceae It is, however, probable that Cooper's observations are not quite correct, and in *Phlox* also the tapetal nuclei first divide and then the daughter nuclei fuse, but occasionally may remain separate. The material in any case requires reinvestigation

At the tetrad stage the tapetal cells enlarge considerably (Fig 10) Their walls are thin and delicate, as noted by Juel (1915). As the pollen grains develop exine and intine, the tapetal cells lose their walls, and when the pollen grains are 2-nucleate and the fibrous endothecial layer has fully differentiated their cytoplasm flows in between the pollen grains, forming a false periplasmodium (Fig. 12) Ultimately this is absorbed by the developing pollen grains. The tapetal nuclei degenerate early, even before the formation of the plasmodial mass (Fig. 11). They begin to stain deeply, assume irregular outline and their fragments float into the plasmodium. In forms with a true periplasmodium, such as the several Helobiales (Sâné, 1939) and Commelinaceae (Tischler, 1915), the nuclei of the tapetal cells are still perfect and living when they float in the plasmodial mass and sometimes even divide mitotically in this condition as noted by Narsimhamurty (1938) in *Rhoeo* and *Zebrina* Similar development of a false periplasmodium has been observed by Juel (1915) in *Cobaea scandens*, but he reported its absence in *Polemonium coeruleum*, though he admits that at certain places it appeared to him as though the cytoplasm was flowing from the cells The present investigation shows that the false periplasmodium in *Polemonium coeruleum* develops at a late stage of anther development Perhaps Juel (1915) did not study such old anthers to observe it.

The primary sporogenous cells give rise to a large number of spore-mother cells These undergo the two meiotic divisions in the normal manner The pollen grains are formed according to the *Simultaneous*-type, as usual in dicotyledons, and cytokinesis takes place by furrowing as described by Farr (1920) in *Cobaea scandens* The pollen tetrads are generally tetrahedral The pollen grains after liberation from the mother cells soon round off, greatly increase in size, develop the usual exine and intine and become greatly vacuolate (Figs 12–14), so that the nucleus is pushed towards the outer side. Here the nucleus divides to form a large tube nucleus and a small generative nucleus The latter is separated by a curved wall to form a lenticular generative cell The vacuoles in the pollen grains are gradually filled up, but no more nuclear divisions occur and the pollen grains are ultimately shed in this 2-celled condition (Fig 15) The generative cell by now becomes spindle-shaped. The exine is well developed It is perforated by numerous germ pores (Fig 16) It is thickest before the first division of the pollen grain nucleus and decreases in thickness as the pollen grain matures (Figs 13–15) Similar decrease in the thickness of the exine during the later stages of pollen grain development has also been observed by Brough (1923) in *Styphelia longifolia*, Puri and Singh (1935) in *Digera arvensis* and Kajale (1940) in many other Amarantaceae Brough (1923) and Singh and Puri (1935) think that this is due to the absorption of exine by the developing pollen grains The writer agrees with Kajale that it is merely due to mechanical stretching caused by an increase in the size of the pollen grains.

MEGASPOROGENESIS AND EMBRYO-SAC.

The ovary is superior and trilocular (Figs 17 and 18) as in most members of the family and is situated on a prominent disk. Dawson (1936) thinks that the disk represents a reduced whorl of stamens, because in many Polemoniaceae it is supplied by a set of vascular bundles which correspond to the traces of an inner whorl of stamens The ovules are numerous, axile, anatropous and possess single massive integument, forming a long, more or less curved micropyle (Fig. 18). The nucellus is poorly developed (Figs. 20 and



FIGS 17–25 *Polemonium coeruleum*. Figs. 17-18, transverse and longitudinal sections of the ovary showing the structure and arrangement of the ovules. Fig. 19, primary archesporial cell. Fig 20, megaspore-mother cell dividing Fig. 21, tetrad of megaspores Fig. 22, 1-nucleate embryo-sac and degeneration of the micropylar megaspores Fig 23, 2-nucleate embryo-sac Fig 24, 4-nucleate embryo-sac Fig 25, mature embryo-sac. Figs. 17 and 18, × 29; Figs 19–25, × *ca*. 533

21) Both the megaspore-mother cell and the tetrad of megaspores are covered only by a single layer of nucellus cells. In later stages even these are crushed, so that the embryo-sac is directly surrounded by the integument. As observed by Billings (1901) in several Polemoniaceae, the inner epidermis of the integument develops into an 'embryo-sac tapetum'. Its cells become densely filled with cytoplasm and begin to stain very deeply. It serves the purpose of a nutritive jacket for the embryo-sac.

There is a single hypodermal primary archesporial cell (Fig. 19) and this directly functions as the megaspore-mother cell (Fig. 20). No primary wall cell is cut off. The same feature was observed previously by Jönsson (1879-80) in this species and by Schnarf (1921) in *Gilia millefoliata* The megaspore-mother cell gives rise to a linear tetrad of megaspores (Fig 21), as reported by Schnarf (1921) in *Gilia* The three micropylar megaspores degenerate (Fig 22), while the chalazal one develops into an 8-nucleate embryo-sac as a result of three successive nuclear divisions (Fig 22–25). The development of the embryo-sac in *Polemonium coeruleum*, therefore, corresponds to the *Normal*-type, and does not agree with the *Scilla*-type as Jönsson's (1879-80) observations would lead us to believe We may therefore conclude that in all investigated Polemoniaceae the embryo-sac is of the *Normal*-type.

The mature embryo-sac is broadly spindle-shaped with a somewhat sharply pointed micropylar end (Fig 25) The egg-apparatus has the normal structure. The two polar nuclei meet and fuse in the centre The antipodals are small 1-nucleate cells and disorganise early

DISCUSSION

The origin of the family Polemoniaceae and its affinities among the Archichlamydeae has been a subject for much controversy among the systematists. Wettstein (1924) and Rendle (1925) derive the order Tubiflorae, in which the Polemoniaceae is generally placed, from a form closely related to the Rosales Hallier (1905) traces the ancestry of the Polemoniales from the Primulales and regards Geraniales as a connecting link between the two. Bessey (1915) traces the origin of the Polemoniales from Ranales through Caryophyllales and Primulales He regards the Geraniales as closely related to the Caryophyllales Wernham (1911 and 1912) and Hutchinson (1926) both derive the Polemoniaceae as an advanced type of the Geraniales. Hutchinson (1926) further believes the Geraniales to have been derived from the Caryophyllales, which he considers as a central group giving rise to a number of orders Dawson (1936) from a recent study of the floral anatomy of many members of the family concludes that the Polemoniaceae is more closely related to the Caryophyllaceae than Geraniaceae and represents a line of development proceeding from a 3-carpellate Caryophyllaceous stock prior to the establishment of free central placentation.

It is thus clear that the general opinion seems to be to derive the Polemoniaceae either from the Caryophyllaceae or Geraniaceae and we have to see which view is favoured by embryological evidence. Here we have to admit that our embryological knowledge is yet very imperfect. While the embryology of the Caryophyllales is comparatively well known, we have no knowledge as yet of some phases of the life-history, e.g., embryo development, of the Polemoniales. The known features of the three families are tabulated below.

Character	Geraniaceae	Caryophyllaceae	Polemoniaceae.
(1) Pollen	3-nucleate	3-nucleate	2-nucleate
(2) Tapetum	Amoeboid or periplasmodial.	Secretory	False periplasmodium
(3) Ovule	Anatropous	Campylotropous	Anatropous
(4) Nucellus	Well developed	Well developed	Poorly developed
(5) Integuments	Two	Two	One
(6) Parietal cell	Present	Generally present	Absent
(7) Embryo sac	*Normal* type	Generally *Normal*-type	*Normal*-type
(8) Endosperm	Nuclear	Nuclear	Nuclear
(9) Perisperm	Absent	Present	Absent
(10) Embryo	Straight	Annular	Straight

The table shows that in some features all the families are quite similar, e g , in the presence of nuclear endosperm and *Normal*-type of embryo-sac In other features (one integument, poorly developed nucellus, absence of the parietal cell, 2-nucleate pollen grains) the Polemoniaceae differs both from the Geraniaceae and Caryophyllaceae. Some of these features are common to the Gamopetalae in general In the form of the ovule, structure of the seed and tapetum, however, we find that the Polemoniaceae shows more resemblance with the Geraniaceae than with the Caryophyllaceae The embryological evidence thus seems to support Hutchinson's (1926) and Wernham's (1911 and 1912) views about the origin of the Polemoniaceae from the Geraniaceae Dawson (1936) rejects this view only for the reason that from anatomical study she could find no evidence to substantiate the theory that the 3-carpellate ovary of the Polemoniaceae has been derived by reduction from the 5-carpellate ovary of the Geraniaceae. She did not find any vestigial vascular traces for the lost carpels. Recent work of Arber (1933), however, shows that in the flowers of angiosperms the vascular bundles do not persist after the organs they supplied have ceased to exist. The absence of any vestigial traces for the lost carpels in the gynoecium of the Polemoniaceae, therefore, cannot be regarded as strong evidence against the origin of this family from the Geraniaceae

SUMMARY

The primary archesporium in the anther of ***Polemonium coeruleum*** consists of 3–4 rows of hypodermal cells The inner layer resulting from the first periclinal division of the primary wall cells develops into the tapetum, while the outer layer divides once again to form the sub-epidermal fibrous endothecium and an early disappearing middle layer The nucleus of the tapetal cells divides mitotically about the diplotene stage of P.M.C., but the daughter nuclei fuse again about the cytokinesis stage, so that the tapetal cells ultimately possess one tetraploid nucleus. The tapetum forms a false periplasmodium. The pollen grains are formed according to the ***Simultaneous***-type. Cytokinesis takes place by furrowing. The mature pollen grains are 2-celled and possess many germ pores

The ovules show a single hypodermal primary archesporial cell, which functions directly as the megaspore-mother cell, and gives rise to a linear tetrad of megaspores The chalazal megaspore develops into an 8-nucleate embryo-sac according to the *Normal*-type Jönsson's observations that the embryo-sac in this species develops according to the *Scilla*-type are thus shown to be incorrect.

The embryological evidence favours Wernham's and Hutchinson's views about the origin of the Polemoniaceae from the Geraniaceae

The author is greatly indebted to Dr A C Joshi of Benares Hindu University for suggesting the investigation, providing the material and helpful guidance

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ON THE NEW DIFFRACTION MAXIMA IN LAUE PHOTOGRAPHS

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(Communicated by Prof M N Saha, F R S)

(*Read August, 20, 1940*)

It has recently been reported by Sir C V Raman and Dr P Nilakantan (1940*a*) that a new type of X-ray reflection with change of wave-length has been observed by them in the Laue patterns of diamond obtained with X-rays from a tube with Cu anticathode, the incident beam being nearly parallel to the threefold axis of symmetry of the crystal In a subsequent paper (Raman and Nilakantan, 1940*b*) the theory of the phenomenon has been given by them and in two other papers (Raman and Nilakantan, 1940*c*) the results obtained by them in the case of diamond and crystals of sodium nitrate have been discussed in detail The new X-ray reflections observed by them lie very close to the Laue diffraction maxima due to 111 planes, and the intensity of these spots is found to be dependent on the glancing angle made by the X-rays with these planes The origin of the new X-ray reflections has been interpreted by them to be due to reflections from dynamic stratifications having a spacing identical with that of the 111 planes, but these stratifications are oriented suitably for Bragg reflection by the influence of incident X-rays on the characteristic vibration of the lattice These authors, however, have overlooked the fact that such new diffraction maxima were observed previously by many workers (Friedrich, 1913 and others) This has been pointed out by Knaggs *et al* (1940) Recently Zachariasen (1940) has put forward a theory of the origin of these new diffraction maxima observed in the vicinity of the Bragg reflection of monochromatic X-rays, and Siegel and Zachariasen (1940) have obtained preliminary experimental results in support of the theory put forward by Zachariasen The object of the present paper is to point out certain difficulties in the theory put forward by Raman and Nilakantan regarding the origin of these new diffraction maxima, and also to discuss the difference between the fundamentals of this theory and that put forward by Zachariasen.

According to the qualitative theory given by Raman and Nilakantan, the new X-ray diffraction takes place in the following way·—

When a parallel beam of monochromatic X-rays OP, O′P′ (fig 1) falls on a set of 111 planes the static direction of which is represented by the line AB, if the glancing angle θ_i does not satisfy the Bragg relation, the phases of motion of the different carbon atoms in the characteristic oscillation of the [illegible] are adjusted by the interaction of the incident X-rays in such a way

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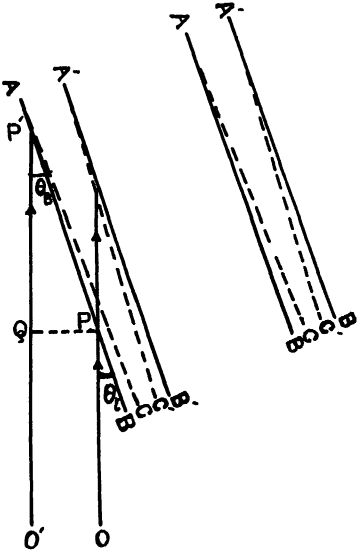
that momentarily all the members of a 111 family of planes are turned till the glancing angle becomes θ_B which satisfies the Bragg relation; a part of the incident quantum is absorbed in exciting the characteristic vibration of the lattice and the remaining part is reflected Thus in this reflection of a new type, the wave-length is slightly changed The change, however, is too small to be observed with X-ray spectrometers It has also been pointed out that this new theory differs from Brillouin's theory in this respect that according to the latter theory of light scattering by elastic waves due to thermal agitation the waves are actually present in the medium and it is possible to pick up for any direction of incidence a Fourier component of the elastic waves having wave-length satisfying the Bragg relation for the incident radiation, but the characteristic vibration of diamond responsible for the new X-ray diffraction has such a large frequency that such a vibration is not excited by thermal agitation and it is excited only when light waves or X-rays are incident on the crystal

There are, however, a few fundamental difficulties about such a hypothesis regarding the origin of the observed new reflections First, when a plane wave is incident on the 111 planes as shown in fig 1, the disturbance reaches P′ earlier than P, and if it is assumed that the difference of phase at the two points causes a rotation of the planes, the direction of rotation should be such that the 111 plane AB should go to the position AC and the corresponding 111 plane A′B′ of the other interpenetrating lattice should come to the position A′C′ shown in the figure In such a picture it has been assumed that the vibration of the lattice of frequency 1332 cm^{-1} which is actually a linear vibration of the two lattices against each other is excited by the incident X-rays earlier at P than at P′ If now θ_i is less than θ^B, the glancing angle for Bragg reflection of CuKα, the orientation AC may give the glancing angle equal to θ_B and so the CuKα may be reflected with the modified frequency θ_i is actually larger than θ_B for CuKβ and so the orientation A′C′ for the 111 planes of the other lattice may produce the suitable glancing angle for Bragg reflection of CuKβ If such a picture be assumed to be correct, one has to further assume that the displacement of an atom at P is of the order of at least one-fifteenth of a millimetre, because the new reflection is observed to take place from a surface of the crystal of dimensions more than a millimetre on each side and in a direction which corresponds to a rotation of the 111 planes from the static position by about 4° It is difficult to believe that such a large displacement of the atom (of the order of 06 mm.) can actually take place in the oscillation of the lattice mentioned above. In fact, investigations of the intensities of X-ray reflections from atomic planes in crystals show that the displacement of the atoms owing to thermal vibration is of the order of a small fraction of the radius of the atom So the displacements due to lattice vibrations are expected to be less than 1×10^{-8} cm But a displacement of the atoms postulated in the theory of the new X-ray diffraction of modified frequency is at least 10^4 times larger than this value.



We can also calculate the ratio of the mean velocity u of the atom to that of the X-rays from the picture of the new type of X-ray reflection given above The maximum displacement of the atom at P takes place in the time in which X-rays travel from Q to P′ If the length PA be taken to be equal to a millimetre and the displacement of the atom at P perpendicular to the plane be assumed to be about ·05 mm the ratio of the velocity $u/c =$ 05 Such a high velocity of the atoms in the crystal seems to be highly improbable

The above arguments hold good even if we assume that only a small volume of the lattice oscillates at a time and the observed reflection is a statistical effect of reflections from different portions of the lattice at different times For any appreciable intensity of the sharp Bragg reflection, the smallest dimensions of the volume contributing to the reflection should be of the order of at least about 25 A.U (i.e , about 10 grating spaces) on each side and in that case the displacement of the atom corresponding to a rotation of

4° is about 1·7 A.U, which again is too large to actually take place in the crystal

Secondly, if the angular displacement of the 111 planes would take place as postulated by Raman and Nilakantan owing to the interaction of the incident X-rays, the amplitude of displacement would have a certain definite value, and the intensity of reflection by these oscillatory planes would not depend on the magnitude of the variation of the glancing angle from the Bragg angle for the reflection of the monochromatic radiation But actually, the intensity of the new spots is found to diminish rapidly with increase in the variation mentioned above

Thirdly, if the new spots are due to Bragg reflection from the dynamic stratifications as suggested by Raman and Nilakantan, it is difficult to understand why the Bragg relation does not hold accurately when the spacings of the 111 planes are taken for calculation In fact, assuming that the Bragg relation holds good for the mean position of the planes corresponding to the initial glancing angle and the angle of scattering, the spacings have been calculated for different values of glancing angles and different values of the spacings have been obtained The reason for this discrepancy is not explained in the theory put forward by Raman and Nilakantan

It has already been mentioned, however, that the appearance of the new maxima in the X-ray diffraction pattern has been observed by various workers, and Zachariasen has recently put forward a theory to explain the phenomenon He has shown that the expression for the intensity of radiation scattered by a simple lattice containing one kind of atoms as modified by thermal vibrations of the crystal contains two terms, the first one giving the Laue diffraction maxima, and the second one the diffuse scattering as given below,—

$$J = J_1 + J_2,$$

where $J_1 = J_0 \ e^{-2M}$ as given by Debye, but J_2 differs from the second term in Debye's expression, and has a maximum in a particular direction

$$J_2 = I_0 \left(\frac{e^2}{mc^2R}\right)^2 \frac{1+\cos^2 2\theta}{2} f^2 e^{-2M} N \frac{4\sin^2\theta}{\lambda^2 m_a v^2} \times \frac{2\pi(NV)^{\frac{1}{3}} Q(\tau_0)}{1+2\pi(NV)^{\frac{1}{3}}\tau_0{}^2}, \quad \ldots (1)$$

where v is the mean velocity of propagation of the elastic waves, θ is the glancing angle of scattering, V is the volume of the unit cell,

$$Q_j = \frac{h\nu_j}{e^{h\nu_j/kT} - 1} + \tfrac{1}{2} h\nu_j,$$

and $\nu_j = \tau v_j$, $\quad \therefore \tau_j = \nu_j / v_j$;

τ_0 is the propagation vector given by the relation

$$\vec{K} - \vec{K}_0 + \vec{\tau}_0 = H_1 \vec{b}_1 + H_2 \vec{b}_2 + H_3 \vec{b}_3,$$

where $\vec{K_0}$ and $\vec{K}$ are vectors in the directions of the incident and diffracted rays respectively such that $K_0 = K = \frac{1}{\lambda}$, $\vec{b_1}, \vec{b_2}, \vec{b_3}$ are vectors representing the inverses of the edges of the cell, and H_1, H_2, H_3 are integers J_2 changes rapidly with the scattering angle and has maximum value when τ_0 assumes minimum values. The direction of maximum intensity lies in the plane of incidence but the glancing angle of scattering is in general not equal to the glancing angle of incidence When $\theta_i - \theta_B = \Delta$, where θ_i is the actual glancing angle and θ_B is that for Bragg reflection, θ_m corresponding to the maximum in diffuse scattering is given by

$$2\theta_m = 2\theta_B + 2\Delta \sin^2 \theta_B \tag{2}$$

This expression shows that θ_m is larger than θ_B if Δ is positive and *vice versa* This has been verified by Siegel and Zachariasen in the case of scattering of CuKα radiation by rock salt, and there is quantitative agreement between the observed values of θ_m and that calculated according to (2) The values of θ_m observed in the case of diamond by Raman and Nilakantan as shown in Table I, reproduced from their paper, agree almost quantitatively with those calculated according to (2), also there is qualitative agreement in this respect that $\theta_m > \theta_B$ when Δ is positive and *vice versa* Again, according to Zachariasen's theory the intensity of the maxima in diffuse scattering diminishes rapidly with increase in the value of Δ and increases with the increase in the temperature of the crystal These effects have actually been observed in the case of diamond by Raman and Nilakantan.

TABLE I.

Maxima in diffuse scattering of Cu radiation from 111 *planes of diamond.*

Glancing angle		$2\theta_B$	$\theta_i - \theta_B = \Delta$	$2\theta_m$	$2\theta_B + 2\Delta \sin^2 \theta_B$
Incidence θ_i	Reflection ϕ				
17° 11′	24° 33′ (Kα)	43° 56′	−(4° 47′)	41° 44′	42° 36′
18° 41′	23° 50′ ,,	,,	−(3° 17′)	42° 31′	43° 1′
20° 49′	22° 43′ ,,	,,	−(1° 9′)	43° 32′	43° 37′
21° 4′	19° 6′ (Kβ)	39° 30′	+(1° 19′)	40° 10′	40° 58′

Thus it is evident that the theory given by Zachariasen can explain the nature of the new diffraction maxima more satisfactorily than that put forward by Raman and Nilakantan The fundamental difference between the two theories is that the diffuse scattering is due to Debye heat waves which are present in the crystal owing to thermal agitation, while according to the latter theory the lattice vibration responsible for the new reflection is excited by the X-rays, and does not exist at ordinary temperatures. The increase in the intensity of the new diffraction maxima with increase of temperature of diamond observed by the said authors probably supports Zachariasen's theory and contradicts the theory put forward by them.

As regards the explanation of the oblique streamers which, as mentioned by Raman and Nilakantan, radiate towards or away from the two Laue spots due to 111 spacings, those authors assume that the streamers arise from the interaction of the vibration of the other two sets of 111 planes on that of one set of these planes, and that they are originated by the modified monochromatic radiation The present authors obtained some Laue photographs of diamond, two of which are reproduced in figs 2 and 3 X-rays were nearly normal to the cleavage plane, i e almost parallel to the threefold axis of symmetry. The photograph shown in fig 2 was obtained with X-rays from a Coolidge tube having tungsten anticathode and operated at 40 K.V. The other photograph was obtained for exactly the same orientation of the crystal but with radiation from a copper anticathode of a Hadding tube operated at about 30 K V The new diffraction maxima due to $CuK\beta$ lie close to the Laue spots due to 111 planes produced by the white radiation and are quite intense but those due to $CuK\alpha$ are the weaker, the further away they are from the Laue spots. These photographs show the reflections from the planes of

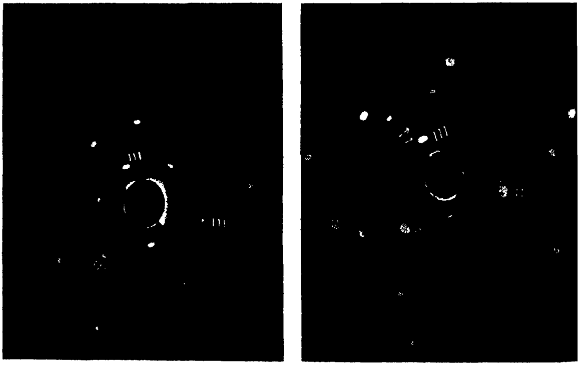


FIG 2

FIG. 3

Laue photographs of diamond.

Fig 2, due to white radiation from W target
Fig 3, ,, ,, radiation from Cu ,,
The spots marked with arrows in fig 3 are due to new diffraction maxima

the three zones 1*kl*, *h*1*l*, and *hk*1, the three 111 reflections being situated at the intersections of the three loops representing the three zones mentioned above. It will be seen by comparing these photographs with those reproduced by Raman and Nilakantan that the directions of the streamers are along the loops starting from the Laue spots due to 111 planes It is, therefore, evident that the planes of reflections producing these streamers are also the planes of incidences on some planes of the crystal which might be imagined to belong to these zones but whose indices are very complicated For a simple lattice the presence of such planes could not be imagined but as diamond consists of two interpenetrating lattices and the 111 planes of the two lattices are very close to each other, being separated from each other by one-fourth the spacing of these planes, some planes slightly inclined to the 111 planes may have some appreciable reflecting power If suitable wave-lengths are used to get the new diffraction maxima from 100 planes, these streamers are expected to disappear

Also the streamers extend up to such large angles from the directions of the static positions of the 111 planes that it is highly improbable that the influence of angular oscillations will extend up to such a large angle

The arguments set forth above show that the new X-ray diffraction maxima observed in the case of diamond cannot be explained satisfactorily by the theory put forward by Raman and Nilakantan and on the other hand some of the observed facts definitely contradict the hypothesis put forward by them The results obtained by them in the case of diamond seem to support the theory of diffuse scattering due to thermal vibration put forward by Zachariasen. The crystals of sodium nitrate contain a large number of interpenetrating lattices and so the interpretation of the results is difficult and is not attempted here.

The authors are indebted to Prof M N Saha, F R S, for his kind interest in the work.

SUMMARY

The qualitative theory put forward by Raman and Nilakantan regarding the new diffraction maxima observed in the Laue photographs of diamond has been examined and it has been shown that there are some difficulties in the assumptions made by the said authors It has been pointed out that the observed facts contradict the theory put forward by them while the theory of diffuse scattering due to thermal vibrations of the lattices put forward previously by Zachariasen can explain satisfactorily all the facts observed by Raman and Nilakantan in the case of diamond The angles made by the directions of maxima in the diffuse scattering with the 111 planes for different angles of incidence agree closely with those calculated from Zachariasen's theory. The streamers radiating from the positions of the Laue spots due to 111 planes of diamond observed by Raman and Nilakantan are shown to be

due to reflections in the planes of incidence of certain complicated planes in the zones $1kl$, $h1l$ and $hk1$.

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2nd August, 1940

DETERMINATION OF THE LIFE OF THE MESOTRON.

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(Communicated by Prof. M N Saha, F R S)

(*Read August 20, 1940*)

INTRODUCTION.

In an attempt to explain the short-range nuclear forces and the anomalous magnetic moments of the neutron and the proton, Yukawa (1935) postulated the existence of heavy particles of mass intermediate between those of electrons and protons. These particles are supposed to be radioactive, so that after a very short time τ, they decay into ordinary electrons and neutrinos. In this respect these heavy electrons or the mesotrons, as they are now called, are quite unique, because while all other fundamental particles are stable they have an extremely short life. It was pointed out by Bhabha (1938*a*) that from the considerations of relativity, the time of disintegration of a mesotron will be longer when the particle is in motion. The life of a particle of total energy E and rest mass μ is given by

$$\tau = \tau_0 \, E/\mu c^2 \qquad .. \quad (1)$$

where τ_0 is the life of a particle at rest.

There are still serious difficulties associated with the heavy electron theory of nuclear forces, however, the actual proof of the existence of such particles in Nature is furnished by numerous cosmic ray experiments. It now seems certain that the penetrating part of the cosmic raidation at sea level consists of particles lighter than protons but heavier than electrons Although it is not yet clear whether the mass of all these particles is the same or it varies continuously or even makes quantum jumps as postulated by Bhabha (1938*b*) and Neddermeyer (1938), it will be interesting to see how far cosmic particles agree in their properties with the nuclear particles postulated by Yukawa. As a first step towards establishing this identity it is necessary to verify whether the mesotrons found in cosmic rays are themselves radioactive as demanded by Yukawa's theory.

Until recently the cloud chamber evidence was rather against the existence of a radioactive decay of mesotrons. Thus Maier-Leibnitz (1939), Neddermeyer and Anderson (1938) and Nishina, Takeuchi and Ichimiya (1939) observed altogether 7 mesotron tracks where the mesotron appeared to come to rest within the chamber, but no trace of the disintegration electron into which it is supposed to decay was visible. Montgomery, Ramsay, Cowie and

[Published December 13th, 1940.

Montgomery (1939) attempted to find evidence of disintegration of mesotrons by counting coincidences between the mesotrons which are stopped by a lead plate and the decay electrons which emerge out of the lower surface of the plate. The results were entirely negative

Very recently in the photographs taken in a randomly operated large cloud chamber, Williams and Roberts (1940) have found clear evidence for the disintegration of mesotrons They have recorded photographically two cases in which mesotrons come to rest within the chamber, and then give rise to high-energy electrons A similar case was reported somewhat earlier by Maier-Leibnitz (1938) although the track of the disintegration electron in this case was not so clear

On account of the rarity of the phenomenon such direct evidence of the disintegration of individual mesotrons are very few There are, however, various indirect evidences Follett and Crawshaw (1936), Ehmert (1937) and Auger, Ehrenfest, Freon and Fournier (1937) found that for the same mass of the absorber, mesotrons seemed to be absorbed more in rarefied substances than in dense materials. According to Euler and Heisenberg (1938) these anomalies can be explained to be due to the instability of the mesotrons predicted by Yukawa In order to penetrate the same mass, mesotrons have to traverse longer distances in rarefied gases like air than in condensed substances like water or lead. In dense materials the range as defined by the energy loss by ionisation may be less than the free path of mesotrons ($L = c\tau$), so that no mesotron is lost due to decay In gases, on the other hand, the range is of the same order as the mean free path L. Some of the mesotrons therefore decay on their way and there is an increased apparent absorption It should be mentioned here that according to Fermi (1940), a part of the mass absorption anomalies may be explained to be due to the effect of density of a material on ionisation loss of a fast particle. According to this idea for a very fast mesotron ($E > 10^9$ e v), with equal masses of the absorbing material, the energy loss in rarefied substances is greater than that in a condensed material This difference increases with the kinetic energy of the particle. However, such an effect is inadequate to explain the total mass absorption anomaly actually observed and one has to fall back upon the disintegration hypothesis

Blackett (1938*a*) showed that it is possible to estimate the life of the mesotron based on the differential absorption of the penetrating component in rarefied and condensed materials as well as from altitude and seasonal variation of cosmic ray intensities. The different methods of determination of the life of the mesotron based on these ideas have been summarised by Rossi (1939). He further showed that the shape of the energy spectrum of the mesotrons at sea level is influenced by the disintegration of the mesotrons. A comparison of the shape of the observed sea level spectrum with the theoretical one seems to justify the disintegration hypothesis. In the following table a summary is given of the work carried out so far, together with the methods used and the results of determination of τ_0.

TABLE I

A Summary of the Previous Work on Determination of τ_0

Observer	Date	Method used	τ_0 in secs.
Blackett	1938(*a*)	Inclination Anomaly and Mass Absorption Anomaly in Water and Lead.	$1{\cdot}7\times10^{-6}$
,,	1938(*b*)	Temperature Effect	$3{\cdot}4\times10^{-6}$
Bernardini, Ferretti *et al*	1940	Altitude Effect at 3·4 Km and 0·5 Km	$5{\cdot}0\times10^{-6}$
,, ,,		Inclination Anomaly	$4{\cdot}0\times10^{-6}$
Clay, Gemert and Clay	1939	Variation of Ionisation at Different Depths of Water	$2{\cdot}0\times10^{-6}$
Euler and Heisenberg	1938	Ratio of Intensities under thick Layers of Air and Water	$2{\cdot}7\times10^{-6}$
Johnson and Pomerantz	1939	Mass Absorption Anomaly in Water and Air	$2{\cdot}6\times10^{-6}$
Nielsen, Morgan *et al*	1940	Altitude Effect and Attenuation Factor	$1{\cdot}2\times10^{-6}$
Pomerantz	1940	Zenith Angle Effect at Sea Level, Integral Method.	$3{\cdot}4\times10^{-6}$
,,		Zenith Angle Effect, Differential Method	$2{\cdot}6\times10^{-6}$
,,		Ratio of Disintegration Electrons to Mesotrons	$6{\cdot}0\times10^{-6}$
Rossi, Hilberg and Hoag	1940	Mass Absorption Anomaly in Air and Carbon	$2{\cdot}0\times10^{-6}$
Rossi	1938	Mass Absorption Anomaly in Water and Lead.	$2{\cdot}0\times10^{-6}$

On account of the great importance attached to the radioactive decay of mesotrons as well as of the large variation in the values of τ_0 obtained by different workers, it was decided to carry out some independent measurements in tropical latitudes

The present paper describes measurements of the vertical and inclined intensities at Calcutta (approximately at sea level and magnetic latitude 12°N) and at Darjeeling (height above sea level 2·2 Km., magnetic latitude 16°N.). We have also estimated the proportion of the disintegration electrons to the mesotrons at the two stations From these measurements, τ_0 the life of the mesotron at rest has been determined by three independent methods, viz.: (*a*) altitude effect, (*b*) zenith angle effect, and (*c*) ratio of disintegration electrons to mesotrons

APPARATUS AND EXPERIMENTAL PROCEDURE.

In the series of experiments described below we have counted coincidences between four Geiger Müller counters in the same vertical plane with their axes pointing magnetic east-west. The two lower counters were shielded by 10 cms. Pb on all sides to cut off the soft component. In order to measure the absorption in lead additional slabs of any required thickness could be placed between the lower counters and the upper. The correction due to accidental coincidences and showers was determined by displacing the second and the third counters from the common axis as shown in figs 1 and 2 With this arrangement no single particle could excite all counters simultaneously This correction varied from about 2 coincidences per hour with no interposed lead to 0·6 coincidence per hour with an interposed lead shield of 10 cms

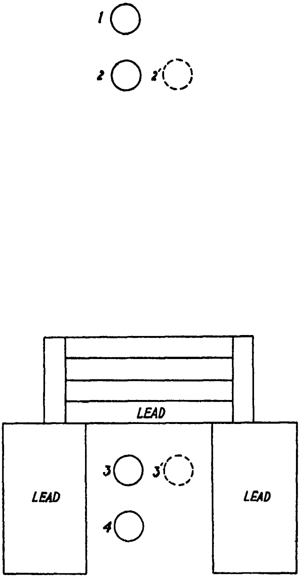

FIG 1

This was mainly due to showers as the accidental coincidence rate was negligible, the resolving time of the circuit being only $1{\cdot}2\times10^{-4}$ sec. In order to measure the inclined intensities, the counter telescope was tilted at 40° to the zenith towards the north.

The principle of these experiments is to compare cosmic ray intensities under the same mass of the absorber traversed in two different directions, so that the actual lengths of paths are different. Since the mass is the same, the ionisation loss will be the same for the two cases and any additional absorption which is observed along the longer track can only be due to decay

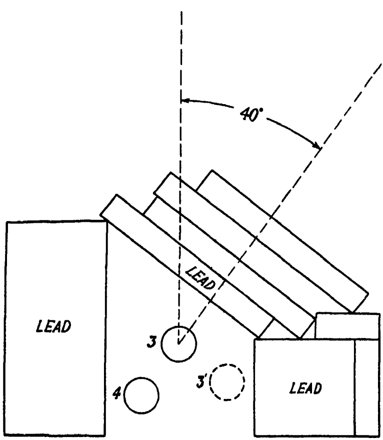

FIG 2

If l be the excess path traversed by mesotrons in one case over the other, and N and N_0 be the intensities observed in the two cases, then the mean free path is given by the equation

$$L = \frac{l}{\log \frac{N_0}{N}} \quad \cdots \quad (2)$$

For the determination of L we have used two different methods.

(a) *Determination of L from Altitude Effect, i e. from the Variation of the Vertical Intensity with Height*

We have compared the vertical intensity of the mesotrons at Calcutta (elevation 200 ft, geomagnetic latitude 12°N) with the vertical intensity at Darjeeling (elevation 2·2 Km, geomagnetic latitude 16° 30′N) The effect of the small difference in geomagnetic latitude may be neglected as the maximum latitude effect at sea level, due to a change of latitude from 40°N to 0°, is not more than 10 per cent according to Compton (1937) and Thomson (1938) In the measurement of the vertical intensity at Darjeeling we have used an additional lead screen equivalent in stopping power to the layer of air between Calcutta and Darjeeling The mass of this layer is given directly by the difference in atmospheric pressure between Calcutta and Darjeeling, i e 1028 − 784 or 244 gms/cm^2 which is equivalent in stopping power to about 34 cms of Pb In this calculation the stopping power of air is assumed to be 1·58 times that of Pb, as given by Bethe, Bloch, Bhabha formula (1938*b*) for ionisation loss. 10 cms of Pb are always used between the counter system as shown in fig (1) to filter out the soft component Hence the vertical intensity under 10 cms Pb at Calcutta is compared with that at Darjeeling under 44 cms The total mass traversed by the rays is then the same in both cases, but the actual paths differ in length In this case the excess path l traversed by the vertical rays at Calcutta is clearly the difference in height above sea level between Calcutta and Darjeeling, that is, $2{\cdot}2\times10^5$ cm With $l = 2\ 2\times10^5$ cm and the measured values of N and N_0 i e the intensities at Calcutta and Darjeeling, the mean free path L may be calculated by means of equation (2).

(b) *Determination of L from Zenith Angle Effect, i e from the Vertical and Inclined Intensities at the Same Station*

For the determination of L in a different way we compared the intensity of the inclined rays ($\theta = 40°$) at Darjeeling with the vertical rays at the same station with an additional layer of Pb between counter system to compensate for the excess mass along the inclined direction. Since the mass traversed by the vertical rays at Darjeeling is about 784 gms/cm^2 the rays inclined at angle 40° to the zenith have to penetrate an excess mass of 784 (sec 40° − 1), i.e. about 244 gms/cm^2 of air over the vertical rays This excess mass is compensated if the vertical intensity of mesotrons is measured under an extra lead absorber 34 cms thick The vertical path through the air and the lead absorber and the inclined path through the air then differ only in actual length but not in stopping power The ratio of the two intensities therefore indicates the mean free path of the mesotrons in air as in the previous case. Hence the vertical intensity of mesotrons at Darjeeling under 44 cms. of Pb was compared with the intensity under 10 cms. at an angle of inclination 40°

to the zenith. The excess path l traversed by the inclined rays in this case is given by

$$l = (Z'_m - Z_1) \sec\theta - (Z_m - Z_1) = 7{\cdot}7 \text{ Km} \qquad .. \quad .. \quad (3)$$

where Z_1 is the height of Darjeeling above sea level, and Z'_m the height of formation of mesotrons incident at an inclination 40° to the zenith.

It is generally assumed that mesotrons are formed in the atmosphere when the mass traversed by the primary rays is about one-tenth of the total mass of the atmosphere. The validity of this hypothesis has been proved by the recent baloon experiments mentioned later in detail. On this assumption the height of formation (Z_m) of the vertically coming rays is about 18·4 Km and that for the rays inclined at an angle of 40° to the zenith (Z'_m) is 20·5 Km. Substituting the values of Z_m, Z'_m and $\sec\theta$ in equation (3) the excess path l in the case of the inclined rays is found to be about 7·7 Km. As before with this value of l and the measured values of the vertical and the inclined intensities, the mean free path for decay may be calculated from equation (2).

RESULTS

The results of determination of the mesotron intensity under the conditions mentioned above are given in the following table. For each case the number of showers recorded per hour was determined by the method of displacement of counters as indicated in figures 1 and 2. The shower rate thus obtained was subtracted from the total number of mesotrons recorded per hour. The corrected mesotron intensity is given in column V, Table II.

TABLE II

Results of Measurements

Observation	Station	Angle to the zenith	Amount of lead between counters	Number of mesotrons recorded per hour, after deducting the correction due to showers
1	Calcutta	0°	10 cms	16·0 ± ·48
2	Darjeeling	0°	44 cms	20·0 ± ·50
3	Darjeeling	40°N	10 cms	14·8 ± ·57

From the results given in Table II it is evident that the vertical mesotron intensity measured under the same mass of the absorber decreases from about 20 to 16 per hour due to a change of height above the sea level by 2·2 Km. Similarly, a tilt of the counter telescope by 40 degrees from the zenith at Darjeeling reduces the intensity of the penetrating component from 20 to 14·8, although the excess mass traversed in each case is compensated by additional absorbers. In both the cases the decrease is much greater than the limits of statistical errors. With the assumption that the reduction of intensities is due to decay of mesotrons along the longer tracks, the mean free paths of these particles have been calculated with the help of equation (2) and are indicated in the third column of Table III.

The mean free path is related to the rest life of a mesotron by means of the equation,

$$L = \frac{c\tau_0 E}{\mu c^2} \quad \text{or} \quad \tau_0 = \frac{L\mu c^2}{cE} \qquad \ldots \quad \ldots \quad \ldots \quad (4)$$

where E is the total energy of the mesotrons considered.

The mesotrons recorded in our measurements are those having energies greater than a certain minimum required to penetrate the ten cms lead screen which is always present. Assuming $\mu = 160m$, i e $\mu c^2 = 8 \times 10^7$ e v it follows from the consideration of ionisation loss of mesotrons in lead $E_{\min} = 2 \times 10^8$ e v In calculating the average energy of the mesotron spectrum at sea level we have, therefore, to consider a lower limit of 2×10^8 e v.

No measurement of complete energy spectrum at our latitude is available We have assumed an average energy of $1{\cdot}3 \times 10^9$ e v which is deducible from the measurements of Blackett (1937) and Wilson (1939) On account of the uncertainty in the actual values of the mass and the average energy of the mesotron beam it is probable that uncertainty in τ_0 is greater than that in L. However, any changes found later in the exact values of these two quantities will produce a corresponding change in the value of τ_0 which can be easily allowed for.

For the determination of τ_0 from the measurement of the vertical intensity at Calcutta and Darjeeling we require the average energy of the mesotrons at Darjeeling This may be obtained by adding to the energy at the sea level the amount spent in ionisation in traversing the column of air between Calcutta and Darjeeling

Thus $$\bar{E}_a = (1{\cdot}3 + 2 \times 10^{-3} \times 244)\, 10^9 = 1{\cdot}8 \times 10^9 \text{ e v}$$

For the second case we require not the energy in the place where the particles are actually observed but the average along their tracks This may be obtained from the formula given by Rossi (1939) and we derive the following average energy for the second case.

$$\bar{E}_b = 2{\cdot}7 \times 10^9 \text{ e.v.}$$

The values of $\bar{E}$ are given in Table III together with those of L τ_0 calculated for each value of L is indicated in the last column of Table III

TABLE III.

Calculation of τ_0.

Method	Data used	L in Km.	$\bar{E}$ in 10^9 e.v.	τ_0 in 10^{-6} secs.
Altitude Effect .	1 and 2	$9{\cdot}86 \pm 3{\cdot}4$	$1{\cdot}8$	$1{\cdot}46 \pm {\cdot}51$
Zenith Angle Effect .	2 and 3	$25{\cdot}7 \pm 6{\cdot}8$	$2{\cdot}7$	$2{\cdot}57 \pm {\cdot}68$

It will be found from the table that the values of τ_0 obtained by the two different methods are in agreement with each other within rather large statistical errors The mean value of τ_0 is about 2×10^{-6} secs

In the next section are described the results of determination of τ_0 by an entirely different method, i.e from the ratio of disintegration electrons to mesotrons at Calcutta and Darjeeling. It is very satisfactory that τ_0 comes out again to be about 2×10^{-6} secs.

DETERMINATION OF τ_0 FROM THE RATIO OF DISINTEGRATION ELECTRONS TO MESOTRONS

Euler and Heisenberg (1938) deduced the following relation for the proportion of the disintegration electrons to mesotrons

$$k = \frac{9X_0\mu c^2}{8\tau_0 cE_c} + \frac{\mu c^2}{2ah} \qquad . \ (5)$$

where X_0 the characteristic unit for air = 275 m , E_c is the critical energy for air $1{\cdot}5 \times 10^8$ e v., h the depth below the top of the atmosphere in gm /cm ^{2}, a the energy loss by mesotrons per gm of air (about 2×10^6 e.v) Substituting the values of the quantities involved

$$\tau_0 = \frac{5\ 50 \times 10^{-7}}{(k-20/h)} \text{ secs.} \qquad .. \qquad . \qquad (5a)$$

In the present experiment τ_0 was obtained by determining the ratio (k) of the disintegration electrons to mesotrons at Darjeeling and Calcutta The values of τ_0 thus obtained agree within the limits of experimental errors with the previous determinations This serves as a check on the correctness of the determination of τ_0 by the former methods

For the determination of k we measured the complete absorption curve of cosmic rays in lead, both at Darjeeling and at Calcutta The results which are given in Table IV are shown plotted graphically in fig. 3.

TABLE IV

Absorption in Lead of the Vertical Cosmic Ray Intensity at Calcutta and Darjeeling.

Thickness of interposed lead absorber	0 cm.	2 cms.	5 cms.	10 cms.	20 cms.	30 cms.	44 cms.
Intensity at Darjeeling	39±·75	34·2±·95	25 6±·80	23·4±·50	22·6±·55	20·6±·50	20·0±·50
Intensity at Calcutta ..	21·6±·95	21·0±·80	17·3±·80	16·0±·48	14·9±·80	15·4±·70	

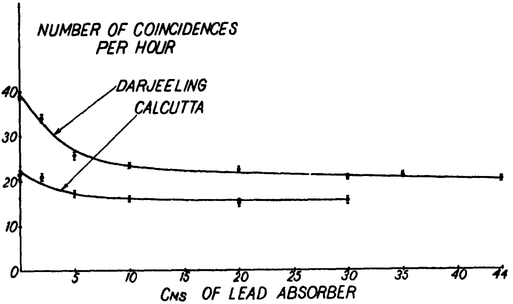

FIG 3

From fig. 3 it is evident that the total intensity of cosmic rays increases by a factor 1·82 due to a change of height of 2·2 Km from Calcutta to Darjeeling Also the proportion of the soft component to the hard increases from 33·4 per cent to 74 per cent between these two stations

The soft component at any place consists of the disintegration electrons (D), knock-on shower electrons (K) and the cascade electrons due to primaries (P) Hence if we denote the total soft component by E,

$$E = D+K+P \quad \ldots\ldots\ldots\ldots \quad (6)$$

In order to determine the fraction of the intensity due to the decay electrons alone (D) we must subtract from the total intensity (E) the effects due to the cascade multiplication and knock-on showers ($P+K$)

From the calculations of Bhabha (1938*b*) the number of knock-on secondaries that accompany mesotrons of energy 10^{10} e v is about 7 per cent of the number of mesotrons If the average mesotron energy is 10^9 e.v the proportion reduces to 5 per cent

The number of electrons expected at Calcutta and Darjeeling due to the cascade multiplication of the primaries can be calculated in the following way In the characteristic units of the radiation theory the distance of Calcutta from the top of the atmosphere is given by $l = 29$, and for Darjeeling $l = 23$. We have next to fix the other parameter, viz. the logarithmic ratio of the energies of the primary and the cascade electrons Due to the presence of the earth's magnetic field only those electrons may be incident on the surface of the atmosphere which have energies exceeding a certain minimum given by

$$E_\phi = 1{\cdot}9\times10^{10} \cos^4\phi \text{ e.v} \quad \ldots \quad . \quad \ldots \quad (7)$$

where ϕ is the magnetic latitude of the place. For Calcutta where the magnetic latitude is about 12°N. the minimum energy of the incident electrons is about

$1{\cdot}7\times10^{10}$ e.v. Only particles with energy greater than $1{\cdot}7\times10^{10}$ e.v. can be incident on the top of the atmosphere at Calcutta. Presumably a bulk of these will have energies just above this minimum limit. If we make the assumption that all the incident particles have energies approximately equal to $1{\cdot}7\times10^{10}$ e.v., then since the critical energy for air is $1{\cdot}5\times10^{8}$ e.v.,

$$y = \log\,(E'/E_c) \approx 5 \tag{8}$$

Bowen, Millikan and Neher (1938) found that the total vertical energy flux at our latitude is 10^9 e.v. per cm.^{2} per sec. This is the total energy carried by the cosmic particles per square cm. per sec. directly overhead at Calcutta. Assuming that all the cosmic particles incident on the surface of our atmosphere have energies equal to the magnetic limit $1{\cdot}7\times10^{10}$ e.v. we calculate the number of particles incident per sec. per sq. cm. to be about 0·058. Since some of the cosmic particles will have energies greater than this minimum value, the above estimate gives the upper limit of the number of particles incident per sec. Johnson (1938) estimates that a more probable number is 0·032. This represents the number of primary particles incident per cm.^{2} per sec. The problem now is to find out how they will multiply in the successive layers of the atmosphere and in particular what intensities are to be expected at Calcutta and Darjeeling.

If $F\,(E'O)$ be the spectrum of the primary particles whose energies exceed E' and $z\,(l,\,y)$ the number of the cascade electrons produced by one primary particle at a depth l and defined by the logarithmic ratio of the energies y, then the intensities of the soft electrons to be expected at Calcutta and Darjeeling after multiplication in the layer of air above these two stations is given by

$$F(E,l) = \int_{E'=E\phi}^{\infty} z(ly)\,\frac{-\partial F}{\partial E'}\,dE' \qquad . \qquad . \tag{9}$$

An exact solution of this equation is difficult and moreover the distribution of the primary electrons is not known with any accuracy. But we can make a simplified calculation on the previous assumption that the energy of all the primary particles is the same. Then from the theories of Bhabha and Heitler (1937), since

$$\left.\begin{array}{l} \text{for}\quad l = 29,\quad y = 5,\quad z(l,y) = 7{\cdot}5\ 10^{-4} \\ \text{for}\quad l = 23,\quad y = 5,\quad z(l,y) = 0{\cdot}03 \end{array}\right\} \quad . \tag{10}$$

the calculated number of the cascade electrons above an energy of $1{\cdot}5\times10^{8}$ e.v. expected at Calcutta and Darjeeling are 0·086 and 3·4 per hour. Taking into account Arley's correction (1938) for the number of slow electrons and the limited solid angle of the apparatus, the number of soft electrons expected to be recorded with our apparatus are about 7 and 0·2 per hour.

It is possible to estimate from the above results the number of ordinary electrons due to decay of mesotrons. The results of these calculations are contained in the following table. The number of mesotrons incident per hour (M) and the total intensity (E) of the soft component at the two stations are given in columns II and III respectively. The estimated values of the number of knock-on electrons (K) and the primary cascade (P), obtained as mentioned before, are given in the next two columns The number of disintegration electrons (D) has been obtained by subtracting ($K+P$) from (E). The two ratios of the disintegration electrons to mesotrons have been given in column VII, and the corresponding values of τ_0 in the last column

TABLE V.

Station	Number of mesotrons per hr. M	Number of electrons per hour E	Knock-on electrons per hour $K = 05M$	Cascade electrons due to primaries P	Disintegration electrons per hour D	Ratio of disintegration electron to mesotrons $k = D/M$	τ_0 in 10^{-6} secs
Darjeeling	23 5 ± 87	16 0 ± 64	1 15	7 00	7 85 ± 64	33 ± ·06	1 8 ± ·3
Calcutta	16 5 ± 48	6 0 ± ·17	82	·20	4 98 ± 17	·30 ± 02	2 0 ± ·2

DISCUSSION

In deriving the life of the mesotrons we had to make the following assumptions It was assumed that mesotrons are the secondaries produced by the primary cosmic particles at a height above the sea level where the mass traversed by the primaries is about $\frac{1}{10}$ of the total mass of the atmosphere. This assumption, which was originally made by Euler and Heisenberg, is based on the observation of Millikan, Neher and Bowen (1937) that at a depth of about 1 metre of water below the top of the atmosphere, the primaries are absorbed more than could be accounted for by the cascade theory It appears that at this height the primaries are absorbed by some other mechanism besides the formation of cascade showers. This additional loss of energy is believed to be due to the formation of mesotrons Although the exact processes which lead to the creation of mesotrons are not yet clear, the recent baloon experiments of Schein, Jesse, and Wollan (1940) and Dymond (1940) seem to confirm these ideas in a striking manner The variation of the mesotron intensity with height above the sea level indicates that the mesotron intensity reaches a maximum value at a pressure of 8 cm Hg, after which the intensity decreases again with height.

The determination of τ_0 from the altitude effect is independent of any assumption regarding the height of formation of mesotrons and also of the assumption of the isotropy of the radiation. It is possibly more correct than the other determination. The agreement between the results obtained by the three methods is therefore very satisfactory.

The second serious assumption in the determination of τ_0 is that the mass of the mesotrons is constant and is about 160 electron masses. The present experimental evidence on this point indicates that the mass lies between wide limits, 100–250 electron masses While it is not impossible that the mass varies according to quantum laws, the experimental errors in the various determinations of mass are so great that they do not exclude the possibility of mesotrons having a fixed mass We have provisionally assumed a fixed mass of 160 m A similar assumption has been made regarding the average energy of the mesotron spectrum at Calcutta which is also not known very accurately. Any changes in the exact values of μ and $\bar{E}$ that are found to be necessary in the light of future experiments will introduce a corresponding change in τ_0 This can be easily allowed for

We have neglected the correction mentioned by Fermi (1940) as this, if present, can account for only a small fraction of the total effect The results of the present experiment therefore give conclusive evidence about the disintegration of mesotrons

It is with great pleasure the writers record their sincere thanks to Prof M N Saha, F R S , for providing facilities for this work at Darjeeling and at Calcutta and also for his continued interest in this work The writers are also indebted to Mr K S Manian for making the counters used in these experiments. We also wish to record our appreciation of the constant help rendered by Mr. B. P. Dutt, Lecturer in Physics, St. Paul's School, Darjeeling.

SUMMARY.

The radioactive decay of the mesotron is confirmed by a series of measurements carried out at Calcutta and at Darjeeling (2 2 Km 16°N., geomagnetic latitude). The vertical intensity of the mesotron at Calcutta has been compared with that at Darjeeling under additional lead blocks equivalent to the mass of air between the two stations. We have also compared the vertical intensity at Darjeeling under 44 cms of lead with that at an inclined direction of 40° to the zenith. Under this condition the mass traversed by the vertical and inclined rays is the same. From these as well as from the ratio of the soft to the hard component at the two stations, the life of the mesotron at rest is deduced to be about $2{\cdot}0\times10^{-6}$ sec. This is comparable with the results obtained previously by different observers.

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Fourteenth Ordinary General Meeting.

The Fourteenth Ordinary General Meeting of the National Institute of Sciences of India was held at 11 A M on Tuesday, the 20th August, 1940, in the hall of the Royal Asiatic Society of Bengal, 1 Park Street, Calcutta

The following Fellows were present —

Bt -Col. R N Chopra, *President*, (in the Chair)
Prof J N Mukherjee, *Additional Vice-President*
Dr B Prashad, *Additional Vice-President*
Dr B S. Guha, *Honorary Treasurer*
Prof S R Bose
Dr H Chaudhuri
Capt S C A Datta
Rai Bahadur Dr S L Hora
Prof P K Kichlu
Dr R B. Lal
Prof P. Neogi.
Major C L Pasricha
Prof M N Saha
Prof N R Sen
Dr A. C Ukil.
Prof S P Agharkar, *Honorary Secretary*

Besides the Fellows there were also some visitors present

1 The minutes of the Thirteenth Ordinary General Meeting, held on the 11th and 12th March, 1940, were read and confirmed.

2. The following Fellow signed the duplicate obligation and was admitted as a Fellow under Rule 13—

Major C L. Pasricha

3 The following papers were taken as read owing to the absence of the authors ·—

(1) Structure and development of the ovule and embryo-sac of *Lasiosiphon eriocephalus* Dcne. By S B. Kausik. (Communicated by Dr A C. Joshi)

(2) Measurement of coefficient of reflection and phase for sound waves By Miss Chandra Kanta (Communicated by Dr. R. N. Ghosh)

(3) The nitration and halogenation of 8, methoxy- and 8, hydroxy-coumarins. By B. B. Dey and Miss V. Ammalu Kutti.

(4) A contribution to the embryology of the Amarantaceae By L B. Kajale. (Communicated by Dr A. C. Joshi.)

(5) Male and female gametophytes of *Polemonium coeruleum* Linn , with a discussion on the affinities of the family Polemoniaceae. By Y. Sundar Rao. (Communicated by Dr. A. C. Joshi.)

(6) The determination of soil constants at broadcast and ultra-high frequencies By Imtiaz Ahmad Ansari, B D. Toshniwal and G R. Toshniwal (Communicated by Prof M N Saha.)

(7) On null geodesies and null corpuscles in the theory of relativity. By C G Pendse (Communicated by Prof S P Agharkar)

4 The following papers were read and discussed.—

(1) New diffraction maxima in Laue photographs By S. C Sirkar and J Gupta (Communicated by Prof M N Saha)

(2) Determination of the life of the mesotron. By N N Das Gupta and P C Bhattacharya (Communicated by Prof M N Saha)

(3) The nature of the colouring substances in coloured Polyporaceae By S R. Bose.

Owing to an engagement the President left the meeting while the papers were being read nominating Prof M N Saha to the chair for the remaining period of the meeting.

The meeting terminated at about 12-30 P M with a vote of thanks to the chair

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